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Polarographic and electro-chemical investigations in the perinaphthenone system

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POLAROGRAPHIC AND ELECTRO-CHEMICAL INVESTIGATIONS IN THE PERINAPHTHENONE SYSTEM.

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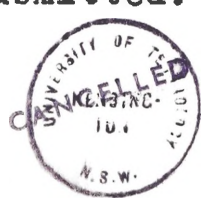

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SECTION A.

INTRODUCTION AND ADVANCED SUMMARY.

The semi-aromatic character (conjugation of the carbonyl double bond with unsaturated hydrocarbon groups forming a fused ring system with some aromatic properties) of perinaphthenone is known. It was thought of interest to examine some of its reactions by physicochemical methods. The electrolytic reduction processes of perinaphthenone, some of its derivatives and benzanthrone (another semi-aromatic ketone) in conjunction with that of benzalacetophenone (chalcone, a $\beta\gamma$ unsaturated ketone) investigated by Pasternak (1) was compared with other properties of these ketones, such as the stability of the free radical, their ease of protonation and their chemical reactivity.

The reduction processes and relative stabilities of the free radicals were investigated by examining the polarograms under different conditions and in the case of perinaphthenone by comparing them with the results of large scale reductions at the potentials of the polarographic plateaus. In alkaline solutions the actual stability of the free hydroxy perinaphthyl radical ion was determined from the redox potential changes of the solution. The ease of the protonation was estimated by determining colorimetrically the dissociation constant of the conjugate acids of the ketones. The information on chemical reactivity was collected from various sources and is described in Section B.

Since reduction of perinaphthenone frequently proceeds through a dark coloured intermediate (2, 3, 4) and Clar and Stewart (5) isolated the acetoxy, benzoxy, and methoxy perinaphthyl radicals, attempts were made to isolate the hydroxy perinaphthyl radical. This proved impossible since in its most stable form (the anion) its rate of decomposition (bimolecular) was found to be 1 millimole^{-1} 1 sec^{-1}.

SECTION B.

CHEMISTRY OF PERINAPHTHENONE.

Perinaphthenone-7 also described as Benzonaphthene-1-one, pyrene-ketone, perinaphthindenone-1, or 1-oxo-perinaphthinedene belongs to a class of compounds, exhibiting properties somewhat in between those of aromatic ketones and quinones to which the term "semi-aromatic ketones" is usually assigned (5). It is intended to compare in this Section some of its reactions with those of benzanthrone, another member of this class, and chalcone (or benzalacetone) a closely related unsaturated aromatic ketone. Their structures are shown in fig. 1.

Perinaphthenone is usually prepared by a modification of the Benzanthrone synthesis; Glycerine and α-naphthol are condensed by the action of sulphuric acid and an oxidizing agent (preferably nitrobenzenesulphonic acid) (2,3) alternately acrolein (normally formed in situ from the glycerine and sulphuric acid) may be condensed with α-naphthol by the action of Hydrogen fluoride (6, 7). Both of these methods are analogous to the Skraup synthesis. Alternate methods are the ring closure of 2, (1-naphthyl) propionic acid chloride, or 1-cinnamoyl naphthalene, by Aluminium Chloride (8, 9, 10, 11, 12). The original preparation is due to Bamberger and Philip (13) who obtained it by the dry distillation of the Barium salt of the

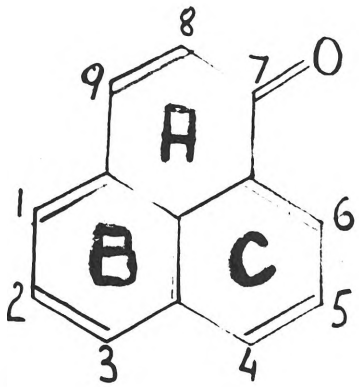
dicarboxylic acid formed during the oxidation of Pyrene.

The product used in this work was obtained by a modification developed by Dr. Silbermann of the method proposed by Luttinghaus and Kacer (14), where α naphthyl-methyl ketone is condensed with ethyl formate in presence of sodium ethylate; ring closure being effected by sulphuric acid.

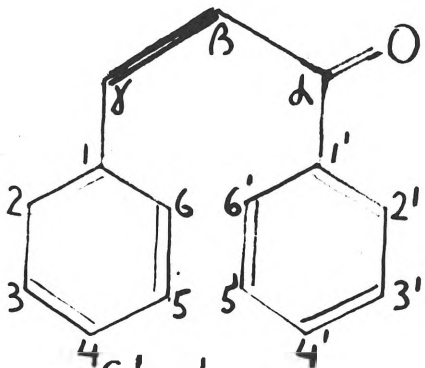
Perinaphthenone dissolves in concentrated hydrochloric, sulphuric and perchloric acids to form orange oxonium salts and reacts with ferric, stannic, and antimonic chloride (all strong "Lewis acids") to form addition products of a similar type. This basicity is stronger than that of chalcone or benzanthrone (which do not react with hydrochloric acid).

On reduction with sodium hydrosulphite Fieser and Newton (15) observed the formation of a red vat; Hydrogenation with Raney nickel catalyst yields the saturated alcohol perinaphthanol-7 (3), using copper chromite catalyst and higher pressure perinaphthanol-7 and perinaphthane are obtained (3), but in presence of Adams catalyst (platinum Oxide) an unstable , bimolecular product is formed (3). Bimolecular reduction ([redacted]) also proceeds at high temperature with Zinc dust in presence of Zinc and Sodium chlorides to give peropyrene, where initial dimerization must proceed at carbon atom 6. The reactivity of this carbon atom is also shown by the addition of Grignard

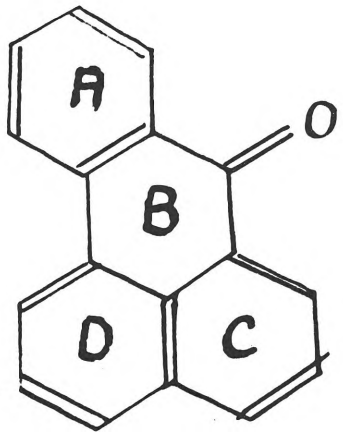
Fig. 1



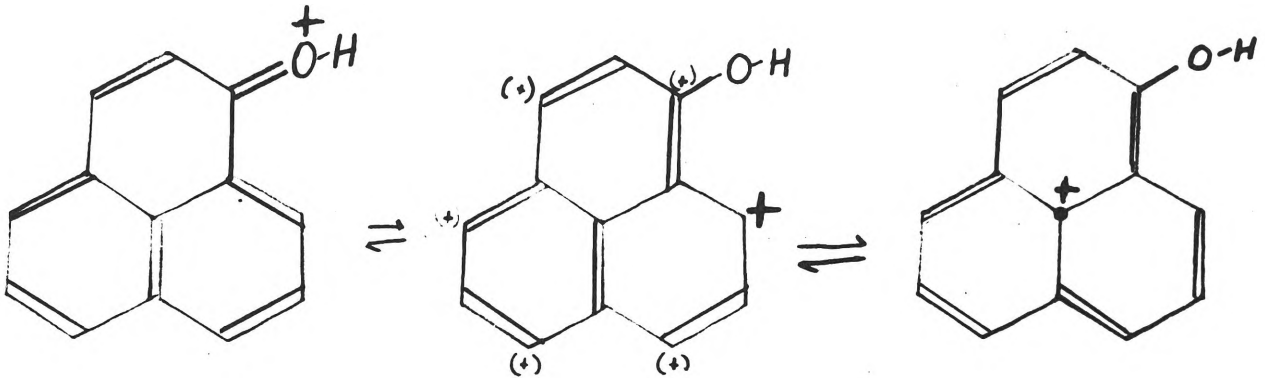
Perinaphthenone



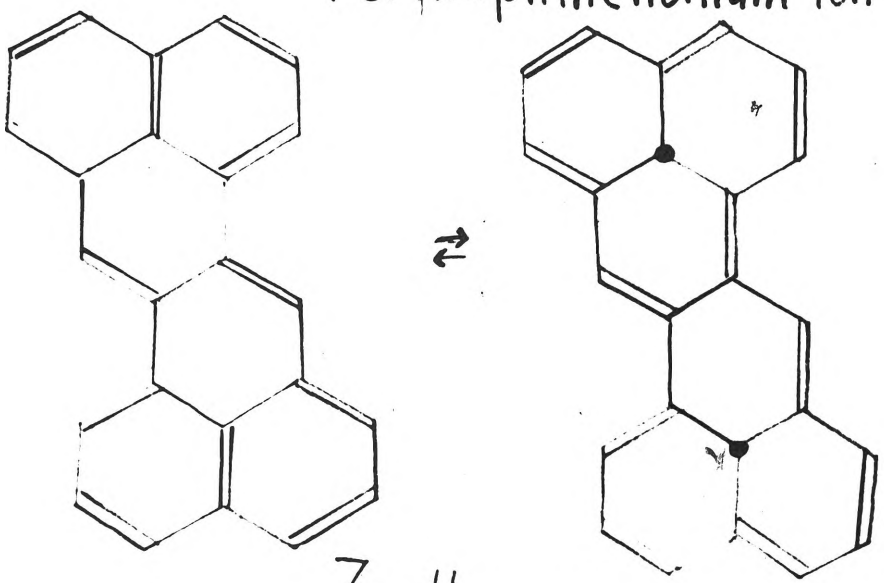
Chalcone



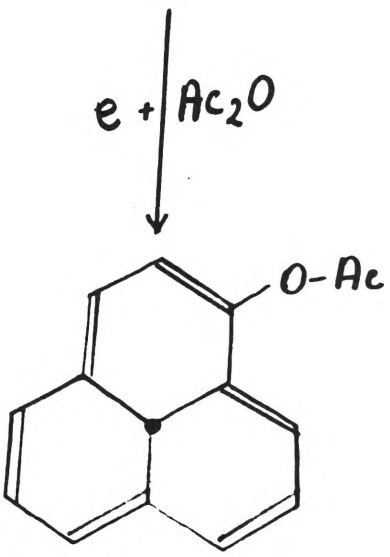
Benzanthrone



Perinaphthenonium ion

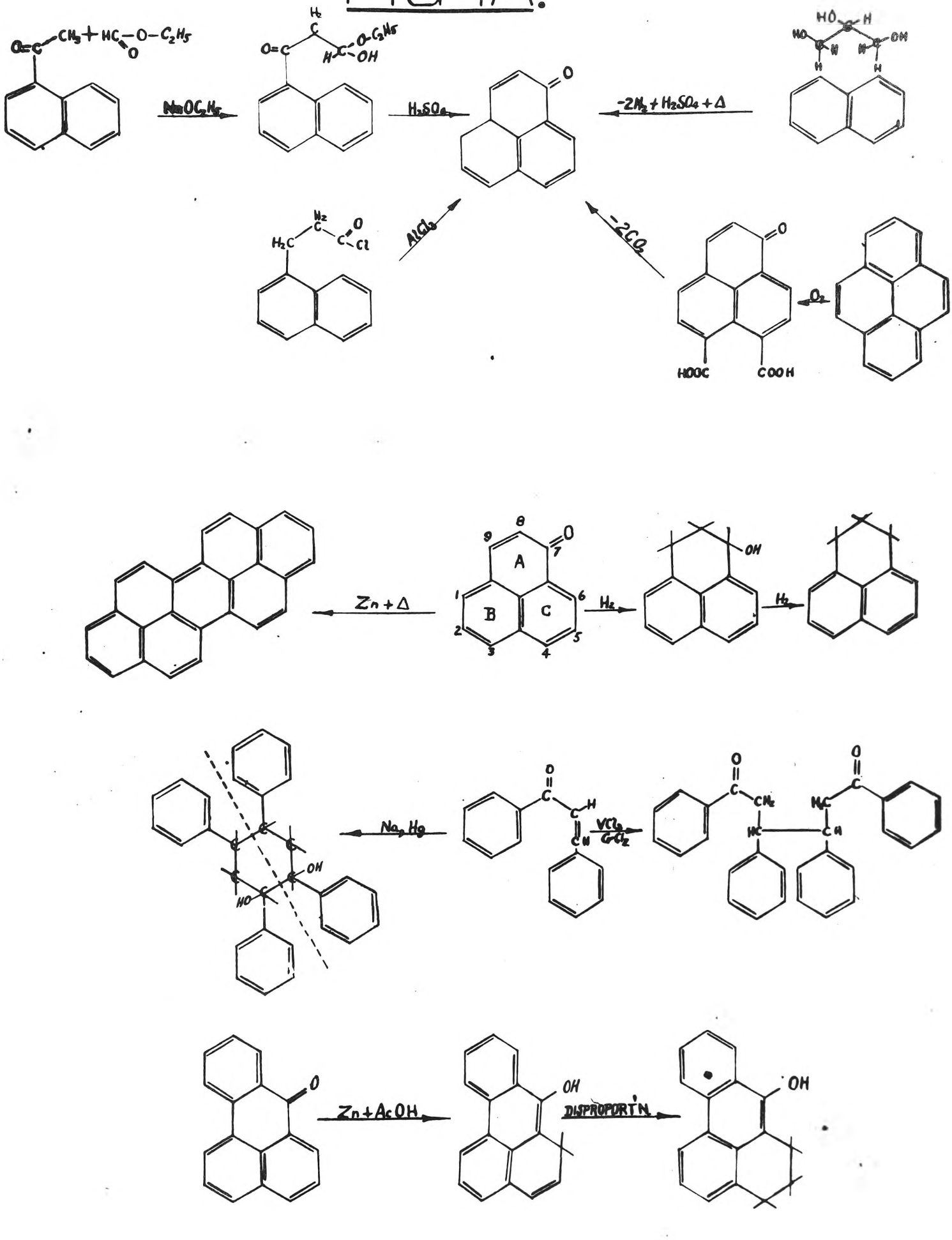


Zethrene



Stable free "Perinaphthyl" radical

FIG·1A.


NaOC2H5
H2SO4
-2H2 + H2SO4 + Δ
AlCl3
-2CO2
O2
HOOC
COOH
Zn + Δ
H2
H2
A
B
C
Na, Hg
VCl3
CCl4
Zn + AcOH
DISPROPORT'N
OH

reagents in this position (4), (16). Reduction of 9-methoxy-perinaphthenone with Lithium Aluminium Hydride will saturate ring C completely forming a β naphthol derivative (17).

Clar and Stewart (5, page 431) found that the acetyl and benzoyl derivatives (esters or methyl derivative (ether) of the carbonium ion of perinaphthenone (fig. 1) are easily reduced by magnesium in ether or less easily in methanol to form a blue free radical. They explain its stability on the assumption that the free electron is localized at the center carbon, leaving the outside carbon atoms in a symmetrical arrangement analogous to the two Kekule structures. This will strain the fourth valency bond of the central carbon atom (which would be at an angle of 90° in respect to the other three bonds). Dimerization will therefore proceed reversibly in the cold, but on warming, the free electron will be delocalized so as to include six of the outer carbon atoms in its possible positions; dimerization will then follow irreversibly as the new carbon-carbon bonds will be quite stable. Similar arguments have been used by Clar to explain the instability of perinaphthene to oxidation and the reactions of Zethrene. Attempts to obtain the hydroxy-perinaphthyl free radical (i.e. with a hydroxy instead of a methoxy, acetoxy or benzoxy group) in strongly acidic solutions during this work were unsuccessful, probably because of internal hydrogen bonding

This would be additional to the strained carbon-carbon link in the center and may well prevent its breaking.

Comparing the reductions of Chalcone with those of perinaphthenone we find that a larger number of dimerizations takes place, particularly of the γ and to a smaller extent at the carbonyl carbon atoms. For example Schneidewind (18) Finch and White (19) and Conant and Cutler (20) all obtain 1, 6,-dioxo, 1, 3, 4, 6, - tetraphenyl hexane using vanadous chloride, chromous chloride, or zinc and acetic acid. Pasternak (1) also obtains this product by electrolytic reduction both in acid (pure) and alkaline media (together with benzylacetophenone). In these reactions the initial free radical formed has its free valency on the γ carbon atom. Sodium amalgam in dilute acid gives, besides the monomolecular product, 1, 2, 4, 5 tetraphenylcyclohexanediol 1, 2 (18) (dimerization at both α and γ carbon atoms). Stronger reducing agents, for example hydrogen on platinum (21), hydrogen iodide and phosphorus (22), yield monomolecular reduction products such as benzylacetophenone, diphenylpropanol or diphenylpropane.

Benzanthrone, like perinaphthenone gives a vat on reduction with alkaline hydrosulphite, but the vat is more stable (23). With Zinc and acetic acid it gives (like 9-phenylperinaphthenone-7 (4)) a colorless dihydro-compound with the intermediate formation of a red free radical (or

possibly quinhydrone) (7). In alkaline conditions, on warming, the dihydrocompound disproportionates to give a 1-10-trimethylene 9-hydroxyphenanthrene. This compound is also formed by the direct reduction with Zinc and Hydrochloric acid, Zinc and caustic soda, or catalytic hydrogenation.

Benzanthrone dissolves in strong sulphuric acid and gives addition products with Lewis acids. (Ferric and Stannic chlorides) (25). On treating with alkali it yields dibenzanthronyl (5 page 365), linkage occurring at carbon atom 2.

Grignard reagents attack Benzanthrone at carbon atom 4 (26).

It will be noticed that ring C of Benzanthrone is generally easiest to dearomatise leaving a phenanthrene aromatic system with a hydroxy group. Similarly perinaphthenone will tend to allow ring C to be dearomatised leaving the more strongly resonance stabilized naphthol structure rather than a naphthalene one. Chalcone will naturally leave its benzene rings unattacked and react at the γ carbon atom of the chain.

SECTION C.

ORGANIC ELECTROLYTIC REDUCTIONS.

In this section it is intended to deal briefly with the electrolytic reduction of organiccompounds in solutions using large (unpolarized) and small (polarized) electrodes. In the latter part (polarography) the effects of superimposing a small alternatingvoltage on the potentials applied will also be mentioned. As there are a large number of reviews on these subjects (27-32) only the points met in this work will be discussed in any detail.

Electrolytic reductions of organic compounds usually proceed along the following path:-

a) $Org + ne + mH^+ \rightarrow (Org\text{—}H)_m^{(m-n)+}$ (initial reduction product)

b) The initial reaction product (i.r.p.) may -

i) remain unchanged

ii) react with other identical particles i.e. dimerize, disproportionate or polymerize

iii) react with unreduced molecules to form products analagous to quinhydrones.

iv) react with molecules of another solute.

v) react with solvent molecules.

vi) react with the cathode.

vii) break up and the products formed behaving then in any of the previous ways.

The velocity of the initial step (a), if monomolecular, is given from rate process theory (33) as

$$\text{reaction rate} = a \frac{kT}{h} \quad \text{exp.} - \left(\frac{\Delta G_f^{\ddagger} + n\alpha EF}{RT} \right)$$

$\Delta G_f^{\ddagger}$ is the energy of activation for the forward reaction, and α the fraction of the electrode potential E operating between the electrode and the molecule. Similar conditions apply to the backward reaction and under equilibrium conditions the well-known Nernst electrode equation

$$E = \frac{-\Delta G_o}{nF} + \frac{RT}{nF} \log \frac{a\,(ox)}{a\,(red)}$$

OR

$$E = Eo + \frac{RT}{nF} \log \frac{a.(org)}{a\,(i.r.p)} + \frac{mRT}{nF} \log H^+$$

can be obtained from the above equation ("British" nomenclature regarding electrode potentials being used).

It will be noticed that the influence of solvent (solvation energy), other solutes (ionic strength) and electrode surface (adsorption effects) on equilibrium conditions extends even more strongly to the reaction rates as their effect on the free energy of activation may be bigger than on the total free energy change.

As the reaction rates are concentration dependent, ($a = fC$) the backward reaction rate will be decreased if a secondary reaction (b) proceeds at a velocity of similar order. In this case the Nernst equation will not hold and the electrochemical reduction is irreversible.

If two different initial reductions are possible their velocities will follow the same equation. It is often feasible even without changing the free energies (as is often done in ionic reductions by complexing) to direct the course of reduction either way by adjusting their velocities by the cathode potential. To obtain only the product of the initial reduction of lower energy of activation (the"faster"one), the required potential is such that only the net forward velocity of the faster reaction is sufficient to enable it to proceed in the time of contact allowed between the particle and the electrode. At a more negative potential the slower reduction may be made sufficiently fast to carry it to completion.

(1) REDUCTIONS ON LARGE SURFACE CATHODES.

In large scale reductions the total current flowing through the cell may be governed by either the uptake of electrons from the cathode, the supply of electrons to the anode or the "internal resistance". Since the internal resistance will vary only with the cell design, the resistance of the diaphragm separating the anolyte from the catholyte, and their conductivities, all of which are usually constant, the cell current governed by it will obey Ohm's law. Considering that the velocity of anode and cathode reactions is generally affected by similar conditions it will be sufficient to deal with cathode conditions only in this Section.

The rate of uptake of electrons from the cathode will depend on three factors; the supply of reducible material to the electrode, the proportion of molecules reacting and the number of electrons taken up by each molecule.

In the absence of stirring, the number of reducible molecules getting to the electrode surface will be affected by their concentration (forcing diffusion) and the free surface area of the electrode. Thus film formation by the reduction product and adsorption can slow down the reduction rate very severely (for instance (34).

Stirring, sometimes produced internally by the simultaneous liberation of gas, will speed up the reduction rate by mixing the solution and mechanically breaking up some of the films formed. In the experimental work described later it was found that very fast mechanical stirring frequently had the opposite effect. Possibly this was due to insufficient time of contact of the reducible material with the electrode. The effective area of a mercury cathode also was occasionally reduced by breaking its continuity (emulsification); adsorption may be one of the contributing factors.

As the reduction proceeds the concentration of the reducible material will decrease and the current will therefore tend to become smaller unless a different reduction process occurs simultaneously. This dropping off is frequently used to show the completion of a reduction.

It has been shown that the initial path of the reduction, i.e. the proportion of molecules reacting with

the electrode and the number of electrons taken up will depend primarily on the cathode potential. This was already pointed out by Haber (35) in 1899, who obtained different reduction products of nitrobenzene at different potentials; its control therefore becomes the main problem in electrolysis. The older methods usually rely, for this, on the total potential drop across the cell and its internal resistance (electrolyte + cell design) or on the cathode material (which by its hydrogen overvoltage somewhat regulates the most negative potential which can be reached); at present various regulators are available (36), which will keep the cathode potential at any required value.

As secondary reactions are usually very susceptible to the activity of the initial reduction product, their path may be determined by the current density and stirring, (affecting their concentration near the cathode), the material and surface condition of the electrode (affecting adsorption) and the solvent and other solutes (affecting their activity coefficients). Slatterbeck (37) was thus able to vary the yields of isopropyl alcohol and pinacol from the reduction of acetone by changes in these conditions.

(2) D.C. POLAROGRAPHY.

D.C. Polarography developed by Heyrovsky (38) follows the same principles as reduction on larger cathodes with the condition that the current flowing is dependent solely on rate of electron uptake from the cathode (or anode in oxidation reactions) and the supply of reducible material to the electrode is controlled by diffusion only. If current is plotted against the potential of the cathode (usually the potential difference applied to the cell is measured and a correction made) "polarograms" are obtained which show a strong increase ("wave") in the current flowing when the reduction potential of a component of the solution is reached. The current flowing at any potential is thus governed by the concentration of the reducible material, the speed of its diffusion, the effective size of the electrode, and the average number of electrons taken up by each molecule, whilst in the "reduction layer" surrounding the electrode, i.e. the completeness of reduction. On this basis Ilkovic (39) derived the equation for dropping mercury electrodes giving the current flowing at a potential where reduction is complete as

$$id = 607n\, CD^{1/2} m^{2/3} t^{1/6}$$

where n is the number of electrons used up by each particle, C its concentration, D its diffusion coefficient; m is the mass of mercury(mg) leaving the electrode per second and t

is the life time of a drop.

If electrons are taken up in one step only, single waves are obtained. They are then usually divided into polarographically reversible or irreversible ones. Unfortunately, "polarographic reversibility" is not necessarily identical with "chemical reversibility". Generally a polarographic reduction is considered reversible, if the forward and backward initial reactions over the main portion of the wave are faster than the diffusion of the reducible form to or reduced form from the electrode, and any secondary reactions of the initial reduction product are slower than its diffusion from the reaction layer. Under these conditions an electro-chemical equilibrium will be established in the reaction layer surrounding the electrode and the relative concentration of the unreduced and reduced forms will obey the Nernst equation. From this the formula

$$E - E_{\frac{1}{2}} = \frac{RT}{nF} \log \frac{id-i}{i}$$

was deduced (40) where id is the "diffusion current" i.e. the amount of current flowing through the cell due to the diffusion of reducible material when all of it reaching the electrode surface is reduced. This is proportional to the concentration of reducible material whereas i, the current flowing at potential E, is proportional to the amount reduced. $E_{\frac{1}{2}}$ is the potential where the current flowing is half the diffusion current. In reversible reductions, if the diffusion coefficients of the oxidized and reduced forms are the same, it is also the potential where

the concentration of reduced and unreduced material are the same, and is therefore equal to the standard redox potential of this system.

If the rate of the forward reaction at the "reversible" redox potential, i.e. when forward and backward processes proceed at the same speed k_f becomes comparable to (or less than) the diffusion rate, a more negative potential will have to be applied to speed it up so that the quantity reduced (current) remains the same. Under these conditions the backward reaction will be slowed down considerably and polarographically the reduction approaches irreversibility. It was pointed out by Eyring, Marker and Kwoh (41) that under these conditions the wave will become flatter and be shifted to more negative values than the "reversible" potential and the equation

$$E - E_{\frac{1}{2}} = \frac{RT}{\alpha nF} \log \frac{id-i}{i}$$

with $\alpha < 1$ will apply reasonably well. Delahay (42) calculated that k_f has to be bigger than 2×10^{-2} cm/sec for full polarographic reversibility; between values of 2×10^{-2} and 3×10^{-5} the wave was shifted but α is not far from 1, i.e. the shape is unaltered; only if $k_f < 3 \times 10^{-5}$ will wave analysis show irreversibility (cm/sec are used for the rate constant to equate its dimensions to those of diffusion).

"Chemical" irreversibility will have the opposite

effect on the slope and position of the wave from polarographic irreversibility. If the secondary reaction is of the first order, we find from the Nernst equation

$$E - E_o = \frac{RT}{nF} \log \frac{id-i}{(i-Aki)}$$

$$E - E_o = \frac{RT}{nF} \log \frac{id-i}{i} - \frac{RT}{nF} \log (1-Ak)$$

where A is the constant required to change i to the concentration of initial reduction product in the electrode reaction layer and k is the rate constant of the secondary reaction
The slope of the wave will thus still be the "reversible" one but $E_{\frac{1}{2}}$, the half wave potential, will not be identical to E_o, the oxidation-reduction potential; the shift of $E_{\frac{1}{2}}$ depending on the value of k.

If bimolecular secondary reactions occur

$$E - E_o = \frac{RT}{nF} \log \frac{id-i}{i-A^2k(i)^2}$$

$$= \frac{RT}{nF} \log \frac{id-i}{i} - \frac{RT}{nF} \log (1-A^2ki)$$

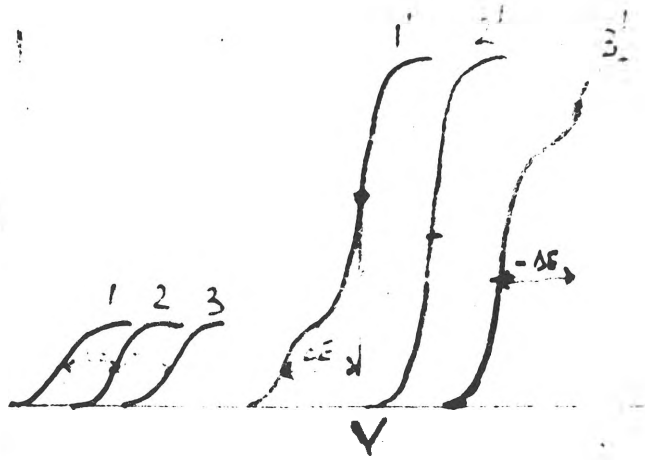
The wave therefore besides shifting to more positive values will also become steeper.

Polarograms of these types (polarographically fully or partly reversible, chemically irreversible) are fairly common for organic compounds (43) and the term "irreversible reduction with a potential determining step" is sometimes used; but the half wave potential will be equal to the redox potential only when the speed of the secondary reduction is slow compared to that of diffusion.

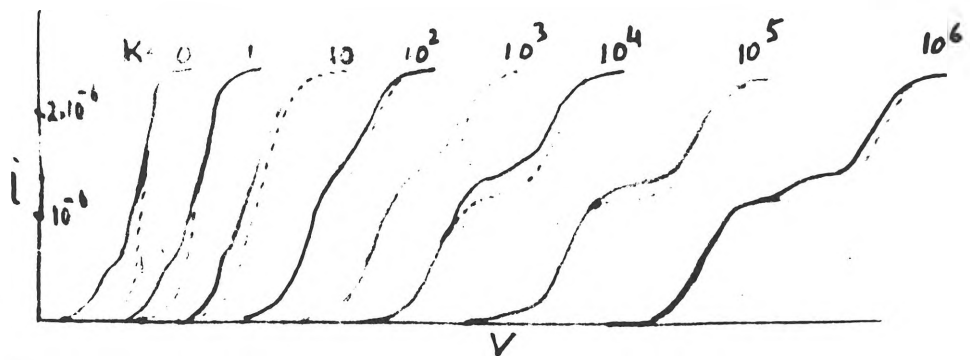
Adsorption of reactant or reaction product by the cathode product will also have a strong effect on the shape and position of the polarogram. Van Rysselberghe (44)

FIG. 2.

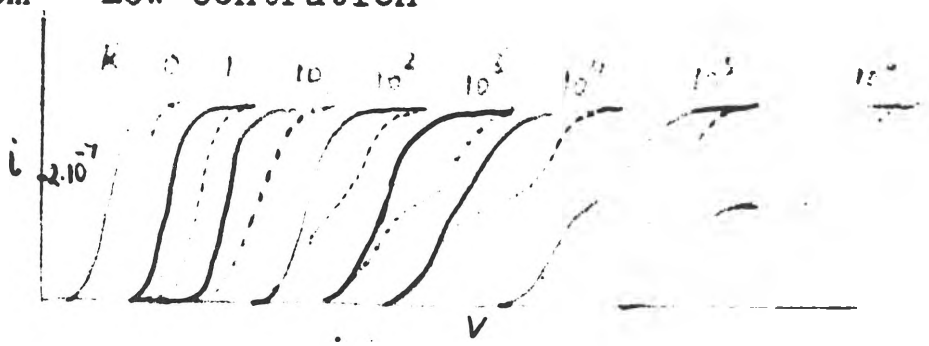
POLAROGRAMS EXHIBITING ADSORPTION WAVES.



Brdička : 1 = adsorption of reduced form
2 = no adsorption
3 = adsorption of oxidized form



Vořišková : polarograms
if semiquinones are formed
K = formation constant
Top - High concentration
bottom - Low centration



____ polarogram if fully reduced form adsorbed

polarogram without adsorption

from results obtained with carbon dioxide deduced the equation

$$E - E_{\frac{1}{2}} = \alpha \frac{RT}{nF} \log \frac{id-i}{i}$$

giving a flatter slope (like "slow" irreversible reductions) on the basis of a reversible adsorption following the Freundlich isotherm of the reduction product on the electrode. This will in effect increase the concentration of reduced material in the "active layer" around the electrode, thus having the opposite effect from secondary reactions.

The half wave potential will then be at a more positive value than the standard redox potential. Brdicka (45), following results obtained on lactoflavine (46) and methylene blue (47) showed that at low concentrations, before the electrode surface is covered, both adsorption of reactant and of product will give flatter waves; adsorption of reduced material will give a wave at a more positive potential (easier reduction, see also (44)) whereas adsorption of the reacting material will shift the wave to a more negative potential (reduction more difficult). At higher concentrations, when the electrode is covered by adsorbed material, these "adsorption waves" will not alter inheight, as adsorption becomes independent of concentration, but normal polarographic waves will be given by the reduction of unadsorbed molecules. Prewaves (if the reduced form is adsorbed) and postwaves (if the unreacted form is adsorbed)

will therefore be obtained. (Fig.2). Casimir and Lyons (48) obtained similar results during the reduction of chinconinic acid.

Some polarographic waves are "rate controlled." In this case the reducible material has to be transformed into an "active form" before reduction takes place and the rate of this transformation rather than the diffusion of inactive material becomes the governing factor (49). If the inactive form is reducible, but at a more negative potential, the rate of transformation will determine the height of the first wave, whilst the rate of diffusion will control the combined wave heights. Brdicka and Wiesner (50), Brdicka and Koutecky, (51) pointed out that the rate controlled current depends on the surface of the electrode ($m^{2/3} t^{2/3}$) which for a given capillary is independent of the mercury level whereas diffusion controlled currents (depending on $m^{2/3} t^{1/6}$) will vary inversely with the square root of the height of the mercury reservoir. Delahay (52) showed that the ratio of the transformation constant to the square root of the diffusion was also important; thus if the reaction is very slow i.e. $KD^{-\frac{1}{2}} < 0.05$ the current is independent of the mercury level as suggested by Wiesner; but when the reaction rate equalises the diffusion rate ($KD^{\frac{1}{2}} < 1.4$) the current approaches inverse proportionality to the square root of the mercury level. Gradations apply to the intermediate ranges. If the initial reduction product rearranges itself

to become again reducible (for instance an enol-ketone change) the rate controlled current will depend on the ratio of the rate of reaction to rate of removal of the initial reduction product from the electrode reaction layer. Miller (53) claims that the reaction layer for this type of reaction has a thickness of the order of 10^{-3} cm compared to 10^{-7} cm if the reaction precedes the electrode reduction (50).

Orlemann and Kern (54) investigated the effect of disproportionation of the initial reduction product, thus reproducing the original reducible material. The current due to the reformed depolarizer $(i - id)$ will depend on the ratio of disproportionation to diffusion of the initial reaction product. At the limit, when disproportionation is very fast, $i = 2id$ and the reduction will appear as a two electron process.

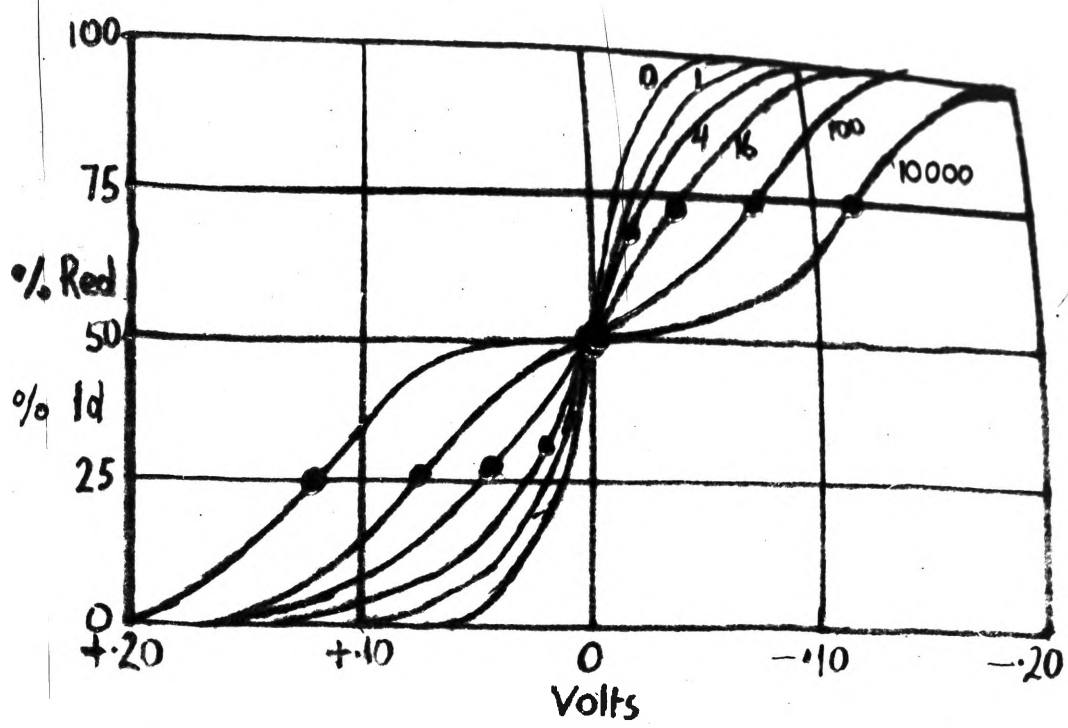
Other types of waves, such as catalytic waves did not occur in the work of this thesis and will therefore not be considered.

When reduction proceeds in two successive stages two waves will be obtained providing the "polarographic reduction potentials" are sufficiently far apart. Again "reversibility" will have an effect on the wave slopes and potentials but other factors such as stability of the

intermediate form may be equally or more important.

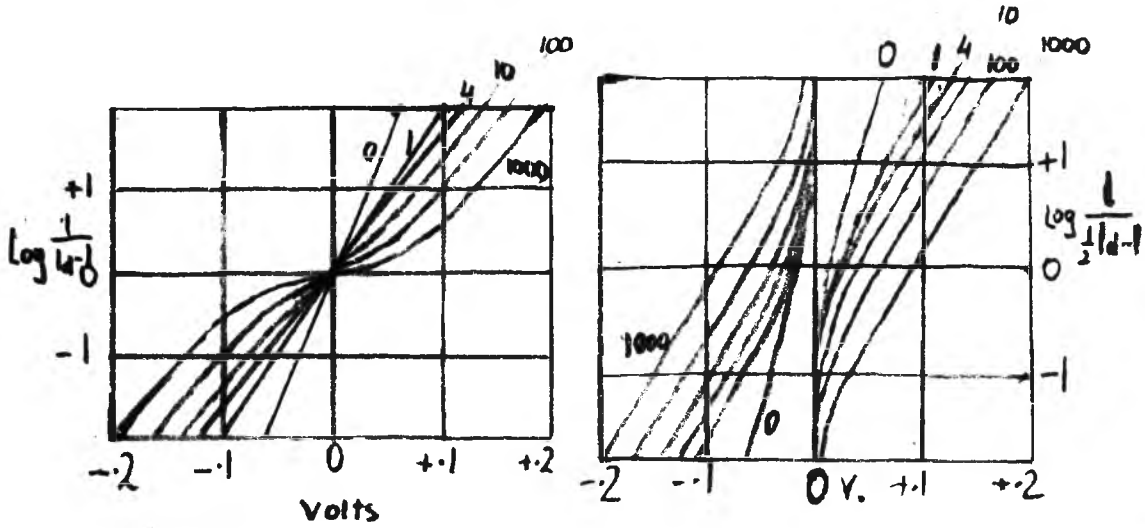
Michaelis (55, 56, 57) developed a series of equations based on the disproportionation constants of semiquinones (the semireduced form of a two electron reduction process) showing the redox potentials of the solution against the total amount of reduction which has taken place if equilibrium conditions, i.e. full reversibility, prevail, and the semiquinone is not directly reduced. From the shape of the curves obtained, particularly from the points of inflexion, it is possible to calculate the stability of the semiquinone to disproportionation or dimerization (quinhydroneformation). (Fig 3) Since, if dimerization occurs the curves vary with concentration and if disproportionation occurs are concentration independent it is possible to distinguish between these two effects (56, 57).

On the basis of these equations Brdicka (58) and Muller (59), both assuming "reversibility", i.e. faster attainment of equilibrium conditions than diffusion, obtained similar theoretical curves for polarograms of these substances. The theoretical polarograms obtained by Muller, and some of their derivatives are also shown in fig. 3. As the stability constant (inverse of the disproportionation constant) increases the two waves become independent and can be considered as separate entities. The distance between the two half wave potentials, which is twice Michaelis'



$$K = \frac{[\text{semiquinone}]^2}{[\text{ox}] \times [\text{red}]} = 0 \longrightarrow 10000$$

● = E_o for red → semiq. and semiq → Ox



Top: Titration (Michaelis) and Polarogram (Muller) of semiquinone forming oxidant

Bottom: Derivative curves of Polarogram (Muller)

index potential E_i can then be used to calculate the stability constant of the semiquinone (if $E_i > 0.06$, $E_i = 0.03 \log K$). The effect of adsorption on the shape of these polarograms was investigated by Voriskova (60), and are shown in fig. 2.

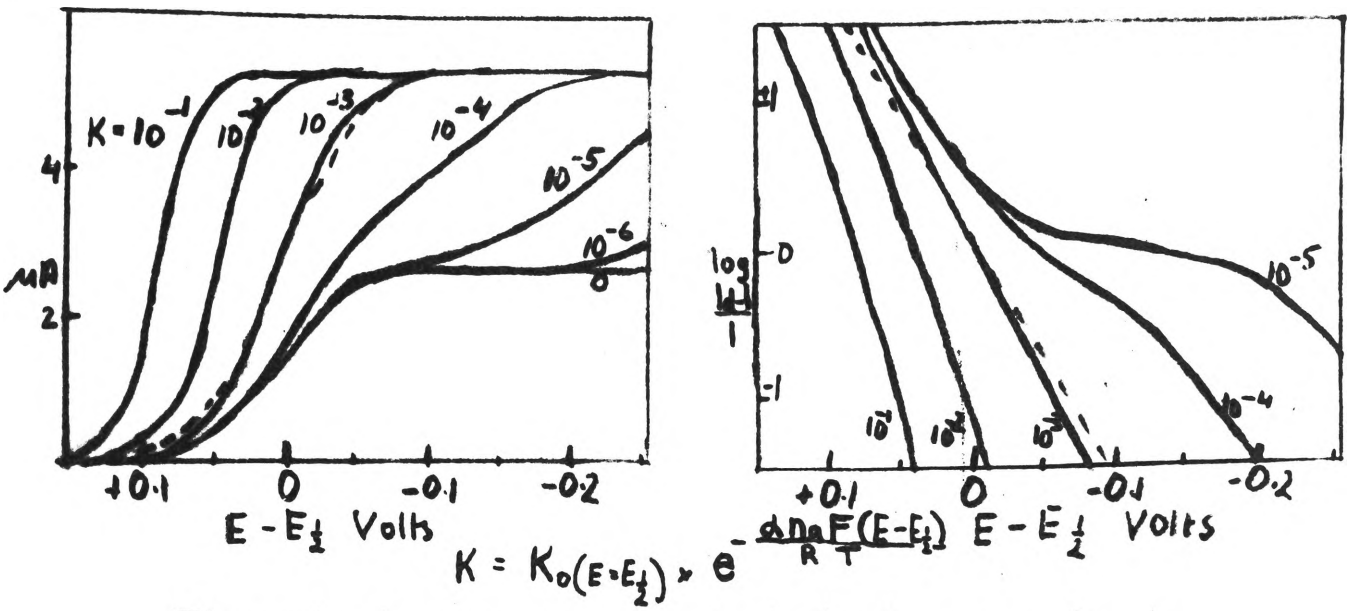
The position of the adsorption waves will depend on which of the three forms present is adsorbed and their concentration at various potentials. Adsorption of the fully reduced compound (fig. 2) produces a prewave for the second step if it is separated from the first step (i.e. the stability of the intermediate is high); otherwise reduction will proceed to a large extent directly, the waves will merge and the prewave will appear at the foot of the combined step as the product is already formed at low potentials. In this case the prewave will be higher than would be expected from the amount adsorbed since some unadsorbed intermediate is produced at the same time. Adsorption of the unreduced material will give rise to a postwave of the first step;it is possible to distinguish it from the prewave of the second step (in the same position) by comparing the size of the residual waves.If the intermediate product is adsorbed a prewave to the first and a postwave to the second wave would be expected; at lower concentration the two waves will be merely spread further apart, showing in effect the higher stability of the adsorbed intermediate.

"Irreversibility", either due to slowness of the electron transfers or to secondary reactions gives rise to various modifications of the position and shape of the waves and only a few examples will be mentioned here. Many others have been described, for instance by Gardner and Lyons (32) and Koutecky (61).

The case of the two slow reactions has been calculated by Berzins and Delahay (62). Assuming a high "over-voltage" (i.e. shift to more negative potentials than the reversible one), which gives a negligible backward reaction, he shows that if k_1 is more than 50 times higher than k_2 two waves will be produced.

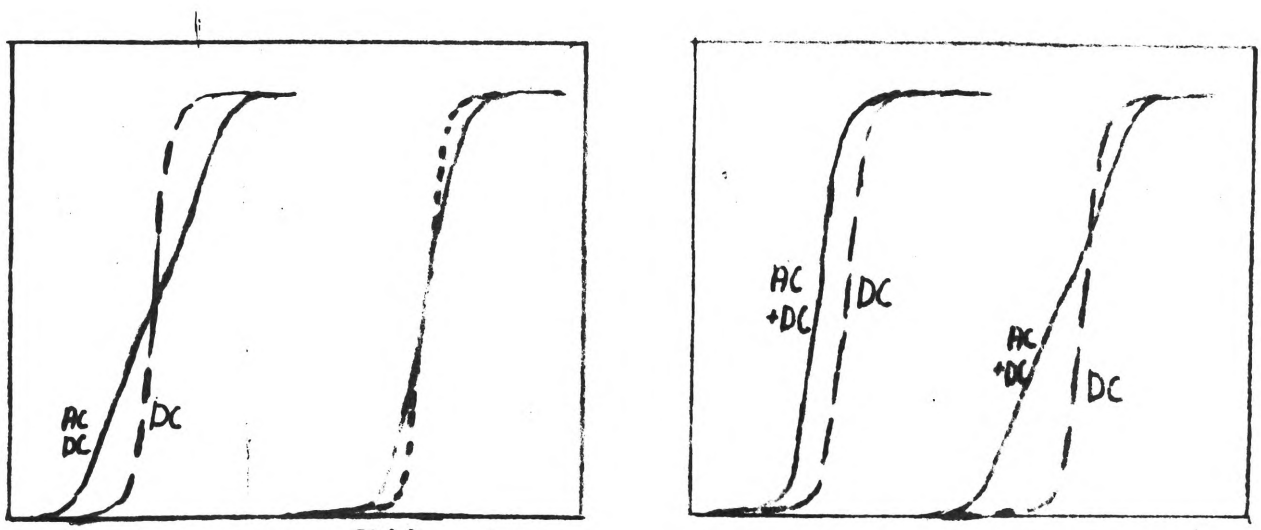
In the same paper Delahay dealt with the problem of a fast "reversible" first reduction followed by a chemically "irreversible" one. This will be described in more detail as the polarographic reduction of perinaphthenone appears to follow this path. The theoretical polarograms are copied in fig. 4. (The values of k given in the graph refer to the rate constant of the second reduction at the half wave potential of the first one. It will be noticed that if the second reaction is faster than the diffusion of the initial product a single wave with steeper slope is obtained at a potential more positive than the "reversible oxidation-reduction" potential of the first wave. This is to be

FIG. 4.



$$K = K_0(E-E_{\frac{1}{2}}) \times e^{-\frac{\alpha n_a F (E-E_{\frac{1}{2}})}{RT}}$$

Theoretical polarogram and derived curve for a reversible reduction followed by an irreversible one
(Berzins + Delahay)



Typical "AC-DC" Polarograms
(Buchanan + Werner)

expected, since the backward reaction does not occur, the equilibrium in the reaction layer is disturbed and the nett forward reaction rate is increased (similar to the case described earlier where no further reduction takes place). As the speed of the second reduction at the reversible redox potential of the first step decreases, the equilibrium becomes less disturbed and the half wave potential of the combined wave will approach the redox potential of the reversible step. Further slowing down of the second reduction will necessitate a more negative potential for it to proceed at a velocity comparable to diffusion; a distorted combined wave, with the top part at a flatter slope than the bottom one will then be formed.

If the second reduction will not occur in the potential range of the first wave two separate, independent waves will be formed, , the first reversible, the second one irreversible and their degree of separation will be determined by the "kinetic reducibility" (the velocity of reduction at the redox potential of its formation) of the intermediate formed. It is only under these conditions that a definite redox potential can be assigned to the potential determining step of a two stage reduction (63) commonly occurring in olefines and ketones.

Large scale reduction at controlled cathode potential will always give the same products as polarographic reduction

at the same potential if no secondary reactions occur and identical solutions and electrodes are used. Polarography will then be the ideal pilot method for larger scale reductions (64). If the secondary reactions are fast (complete before diffusion from the "reaction layer") the same will apply provided the current density is of the same order, so that the concentrations of the initial reduction product when formed are similar. But if secondary reductions are slow completely different results may be obtained as the concentration of their products is negligible in polarography but will build up as large scale reduction proceeds.

Thus, for instance, if disproportionation of the initial reduction product (one electron) is slow and its further reduction proceeds at a more negative potential two equal one electron waves will be obtained. Large scale reduction at the plateau of the first wave will nevertheless produce the two electron product as the initial product, continuously formed at the electrode, diffuses into the bulk and then disproportionates.

(3) A.C. POLAROGRAPHY.

The superimposing of a small sinusoidal alternating voltage upon the potential applied to a dropping mercury electrode will produce interesting effects. If the alternating current flowing through the cell is measured it will be found to rise sharply at different potentials of

the cathode, depending on the solute present, and then fall back. These effects have been investigated in detail by Dr. Breyer and his school. (65, 66, 67).

The curves are caused by a reversible rearrangement of the particles surrounding the electrode at a definite potential. This may be either due to an adsorption-desorption process only of the active substance at that potential or its reduction. The first process, which requires only a dipole in the "depolarizer", will therefore not be accompanied by a D.C. polarographic step and is called tensammetry. In the alternate process (A.C. polarography) the summit potential (peak) will be reached when the rate of rearrangement of molecules following their reduction is at its maximum. It will then coincide with the half wave potential of a reversible reduction where the largest amount of transformation can occur. Although irreversible D.C. reductions of inorganic ions give no A.C. waves, many organic compounds, whose D.C. polarograms are considered irreversible, show them (68), though summit and half wave potentials do not necessarily coincide. The absence of an A.C. wave thus appears to denote "polarographic irreversibility", i.e. an extremely slow speed of the backward reaction (oxidation) at the potential of the D.C. wave. The formation of an A.C. wave on the other hand seems to require only "momentary reversibility", i.e. electrochemical reversibility between the "oxidant" and its initial reduction product. The initial reduction product may dimerize or decompose without destroying the A.C. wave.

(4) A.C.-D.C. POLAROGRAPHY.

If the superimposed alternating voltage is fairly large (100 milli.volts) and the direct current flowing through the cell is measured, A.C.-D.C. Polarograms are obtained; (Buchanan and Werner(69)) they are also illustrated in fig. 4.

Their difference from the normal Polarograms is assumed to be due to rectification of the alternating current. Thus at potentials more positive than the half wave potentials of the fully reversible D.C. wave an excess of reducible materials is present in the reaction layer; this will give a partial rectification of the negative portion causing a more negative potential and hence a larger diffusion current; at more negative potentials the excess of reduced material at the electrode surface will give reverse rectification and thus the effective potential will be less negative giving a smaller diffusion current.

If the reduction is irreversible, the reduced material is unable to act as rectifier and hence only rectification in the negative direction is possible. If the irreversibility is due to a slower change in the initial reduction product some reduced material will still be available and partial rectification of the positive portion of the A.C. will be possible. This effect will increase with higher frequency and the "cross over" potential, where rectification of both

portions is equal and the potential thus unchanged will therefore move from the top of the polarograms towards the centre (70). The above arguments have all been applied to the reduction of a metal ion to a metal; if the reduced molecules remain in solution somewhat different results were obtained which will be discussed later.

SECTION D.

POLAROGRAPHY OF KETONES.

The first polarograms of ketones were obtained by Shikata and Tachi (71). Semerano (72) suggested that the wave of acetone was due to the formation of the carbanion $Me_2\bar{C}$-OH which then yields the alcohol or (by combination with another molecule of acetone) the pinacol. A number of papers (73-80) dealing with the polarography of aromatic and unsaturated ketones were published between 1936 and 1944 but as the pH was not fixed in most cases the half wave or deposition potentials published are only comparable under identical conditions; thus Koelsch and Anthes (4) compared a polarogram of perinaphthenone and 9-phenyl-perinaphthenone in Lithium Chloride. More detailed studies have been carried out by Takazawa and Smith (81), Valyashko and Rozum (82) and Pasternak and v. Halban (83) on acetophenone and its derivatives, by Ashworth (84), Gardner (85) and Bobrova and Sokolow (86) on Benzophenones and by Vodzinskii and Korshunov (87), Geissman and Friess (88) and Schraufstatter and Deutsch (89) on chalcones, flavones, flavanones and other unsaturated ketones. The polarography of tropolones, which show some similarities to semiaromatic ketones, has been described by James and Speakman (90) and Neish and Muller (91).

The generally accepted polarographic reduction mechanism of ketones, based on that of benzaldehyde

proposed by Takuoka (92) and Baker, Davies and Hemmings (93) is given in detail by Ashworth (84) Pasternak (1) and Gardner (85).

An electron and hydrogen ion are taken up reversibly to form a free hydroxy radical which then dimerizes to a pinacol or is further reduced irreversibly to an alcohol.

The position of the first wave will depend on the difference of free energy between the free radical and the ketone and the hydrogen ion activity. Thus aromatic groups (which stabilize the free radical) will decrease the half wave potential (making reduction easier) but a conjugated double bond having a similar effect without disturbing the aromaticity of the structure will be more powerful in that respect.

($E_{\frac{1}{2}}$ at pH1.3 of acetophenone = 1.12, Benzophenone = 0.94, tropolone=0.90, benzalacetone = 0.76, benztropolone = 0.70, Benzalacetophenone = 0.57, Dibenzalacetone = 0.42.) Coulson and Crowell (94) found good agreement between quantum mechanical calculations and the experimental half wave potentials of some unsaturated and aromatic aldehydes and ketones. Electron withdrawing groups in the molecule are known to have a bigger activation effect on the carbonyl than on the hydroxy group and should therefore also make reduction easier whilst electron donating groups should have the opposite effect; Brockman and Pearson (93) using

substituted benzophenones showed this assumption to be correct. Since hydrogen ions are taken up in the reversible reaction the half wave potential should shift to more negative values by 0.06 volts for each increased pH unit. This was found to be the case for benzophenone (85), benzalacetophenone(1) and the tropolones (90,91) as long as the first wave had not merged with the second one; the combined wave shifts only at a slower rate. (0.03V/pH for benzophenone (1)).

Two alternative factors regarding the stability of the free radical govern the position of the second wave but do not seem to have been considered separately.

If the free radical is "polarographically stable", (i.e. its rate of decomposition is slower than its rate of diffusion), then the position of the wave will depend only on the speed with which reduction proceeds at a definite potential. At the half-wave potential this is equal to the speed of diffusion of the free radical. It is usually pH independent, as the addition of the electron is the rate determining step, and will therefore frequently be "caught up" by the first wave as the pH increases. The two waves will then merge, and when the velocity of reduction of the free radical exceeds that of its diffusion at the potential where only a small amount of it is formed(at the start of the reversible first step), its concentration will be decreased and the first wave shifted to more positive potentials. This is the effect mentioned earlier (fig. 4, Berzins and Delahay)

(62)) and accounts for the half wave potential change of less than 0.06V per ^{pH} unit of the combined wave.

Should dimerization or disproportionation be appreciably faster than diffusion of the free radical, a more negative potential will be necessary before reduction can take place and the separation of the two waves will then be an indication of the instability of the free radical.

Day and Kirkland (96), Day, Milliken and Shults (97) and Day and Biggins (98) compared the polarography of Benzophenone and a number of condensed aromatic ketones such as Fluorenone, Anthrone, Xanthone and Benzanthrone in various Hydrogen ion and alcohol concentrations, and considered the tendency towards the formation of fused waves as an indication of the stabilizing power of the aromatic group.

A third wave (frequently described as the second one due to fusion of the first two) may be produced in alkaline conditions at the expense of the second one. Ashworth (84) found that an increased concentration of metal ion present (ceasium being more effective than lithium) decreased its height and shifted its position to more positive values (thus merging the waves again). He suggested that it was due to the formation of metal ketyls; this appears unlikely as they would be completely ionized in aqueous solutions. An alternate suggestion is that dimerization of the anion is slowed down by the higher concentration of smaller ions, allowing the speed of reduction to compete with it already at more positive

potentials.

Unsaturated mixed ketones such as benzalacetophenone (chalcone) also give rise to third (second) waves. These are not at the expense of the previous wave and occur at approximately the potential of the waves of the saturated ketone (benzylacetophenone). Pasternak (1) and Geissman and Friess (88) suggest that the normal second step involves the direct addition of the electron and hydrogen ion to the carbon-carbon double bond yielding the saturated ketone which is then reduced at its normal potential. As the height of the third wave is less than that of the first two and is strongly affected by changes in acidity it seems more likely that the enol is produced first; this will then rearrange to the ketone and the ratio $\frac{h3}{h1 + h2}$ (the two waves of the saturated ketone are usually fused) will indicate the rate of ketonization compared to diffusion.

SECTION E.

EXPERIMENTAL METHODS AND RESULTS.

(1) PREPARATION OF PERINAPHTHENONE.

This preparation was carried out in collaboration with Dr. H. Silbermann.

1.55 g of pulverized sodium were covered with 60 ml anhydrous ether in a round bottomed flask protected from moisture and equipped with an efficient stirrer. To the well-stirred suspension a solution of 8.5 g α-methyl-naphthyl-ketone, and 6.5 g purified ethylformate in 10 ml anhydrous ether was added dropwise over 20 minutes at approx. 5°C. Stirring was continued for 1 hour at 5°C followed by 3 hours at room temperature. The reaction mixture formed a thick yellowish brown suspension of the sodium salt of the oxy-methylene derivative. After standing overnight this was filtered, washed with ether and dried in vacuum. 9 g of this salt were introduced in small portions with good stirring into 90 ml of 84% H_2SO_4 cooled externally with ice water. After the addition stirring was continued for 2 hours at 6-8°C, and 2 hours at 10-17°c. The dark red solution formed was poured onto 50 g of ice. Some resinified material was removed by filtration and the clear filtrate was diluted to approx. 500 ml. The yellow powdery precipitate of perinaphthenone was filtered and well washed with water. Crude yield 80% of theory. It was purified by vacuum distillation and recrystallisation from ethanol. The purified product was a canary colored powder melting at 154.5-155°.

(2) D.C. POLAROGRAPHY.

(a) Method:-

The first polarograms were obtained with a Leeds and Northrup Electro-Chemograph; as their shape and position were found to be insufficiently accurate due to the slow response of its Micro-Max recorder, this instrument was replaced by a manual one. Its circuit diagram is shown in Fig. 5, the essential components being a Leeds and Northrup Students potentiometer, a 999.9 ohms resistance, a Standard Weston cell and a Radiometer Galvanometer with built in shunts giving full-scale deflections from 2-500 microamps. A 2000 microfarad condenser was placed across the galvanometer terminals to dampen oscillations. Accurate and reproducible results were obtained, provided a sufficient period of time was allowed after large current changes to enable the condenser charge to become constant.

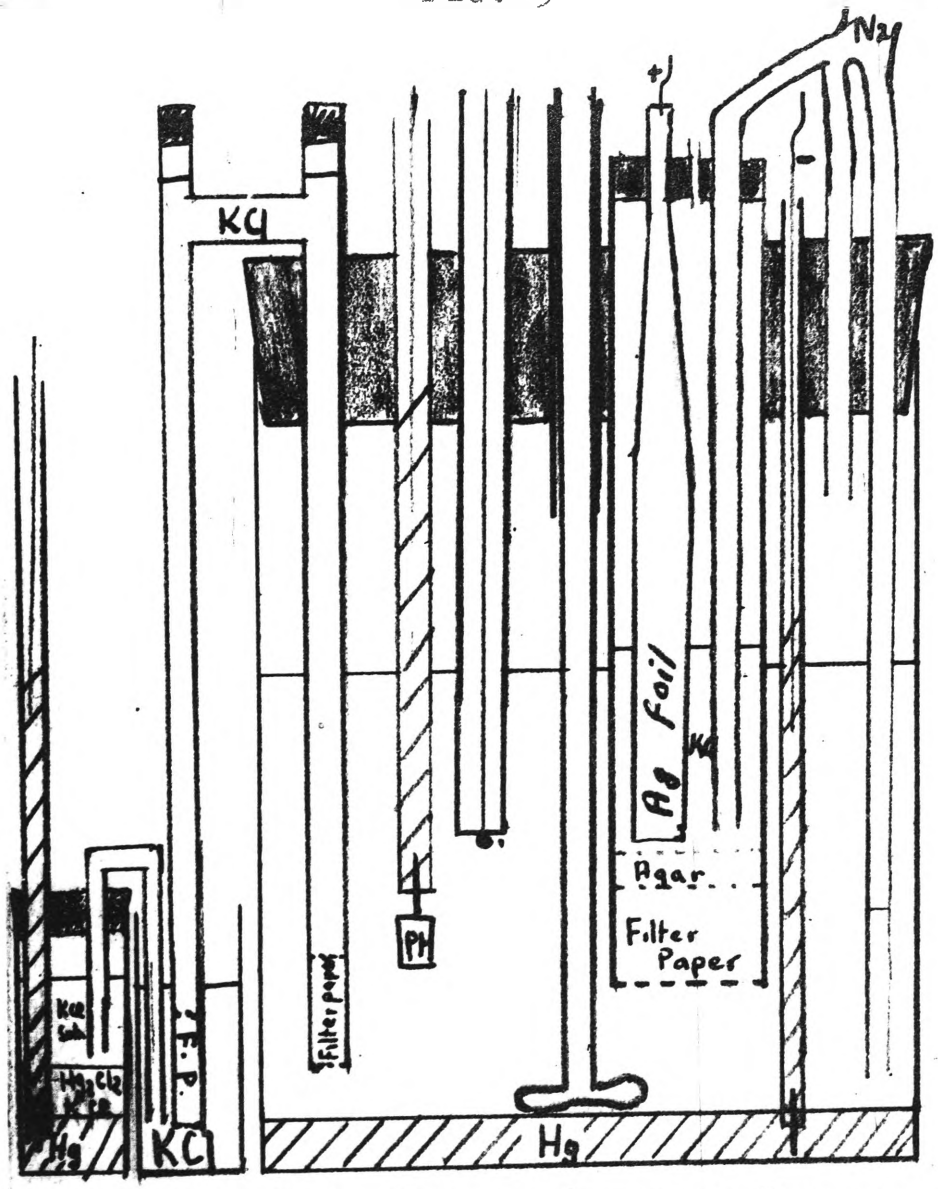
The cells used (except for polarograms during larger scale reductions) were of 10 cc capacity and were connected through a potassium chloride reservoir to the saturated calomel electrode by two H tubes. These were sealed with filter paper plugs and filled with a saturated potassium chloride solution except during the polarography of strongly acidic solutions when a sintered glass connection, filled with a similar solution was used ~~for the cell~~ to prevent the introduction of any hydrolysis products of the filter paper.

The total cell resistance was measured using a Wheatstone bridge circuit and a 1000 cycles alternating current; all cathode potentials tabulated are corrected for the IR drop.

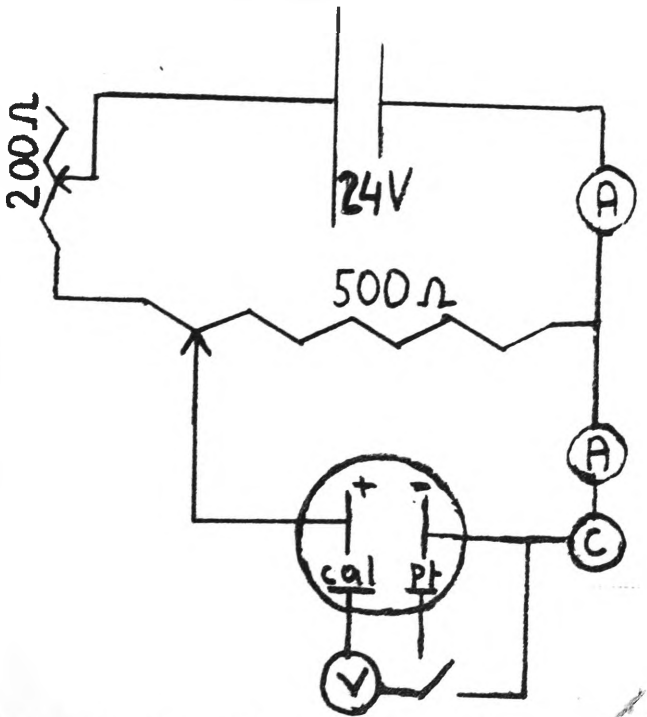
Tank nitrogen, which had been purified by passing through alkaline pyrogallol solution and saturated with the solvent used was bubbled through the solution for 10-15 minutes before and over the solution whilst readings were taken. Four capillaries were used; their characteristics are given in the appendix; they were connected to the mercury reservoir by rubber tubing which was later replaced by polyvinyl chloride. The mercury was purified by washing with Nitric acid and water and finally distilled at reduced pressure.

Prideaux-Ward buffer solutions were used between pH2 and 12. The pH values in water and alcohol (shown in fig.6) were determined using a Hydrogen electrode. The pH values of the alcoholic solutions are therefore "apparent pH" values as no corrections were made for junction potentials or changes in the E_o value for Hydrogen. The aqueous buffer base (0.04M in acetic, boric and phosphoric acids) was made 0.2N in KCl so that the ionic strength did not change significantly as 0.2N NaOH solution was added; for work in 50% ethanol, both buffer base and NaOH were diluted with it. As expected, the ethanol by decreasing the dissociation of the acids, increased the apparent pH by approximately 1 unit. Ethanol which had been standing for a longer period was found to give small waves; it was therefore refluxed with caustic soda to remove aldehydes,

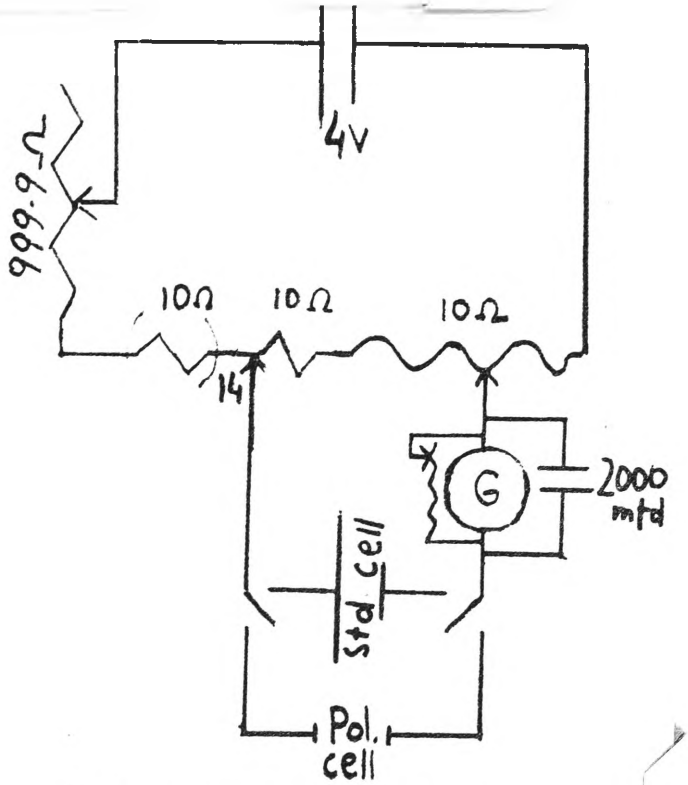
FIG. 5



Cell for Reduction at Constant Potential

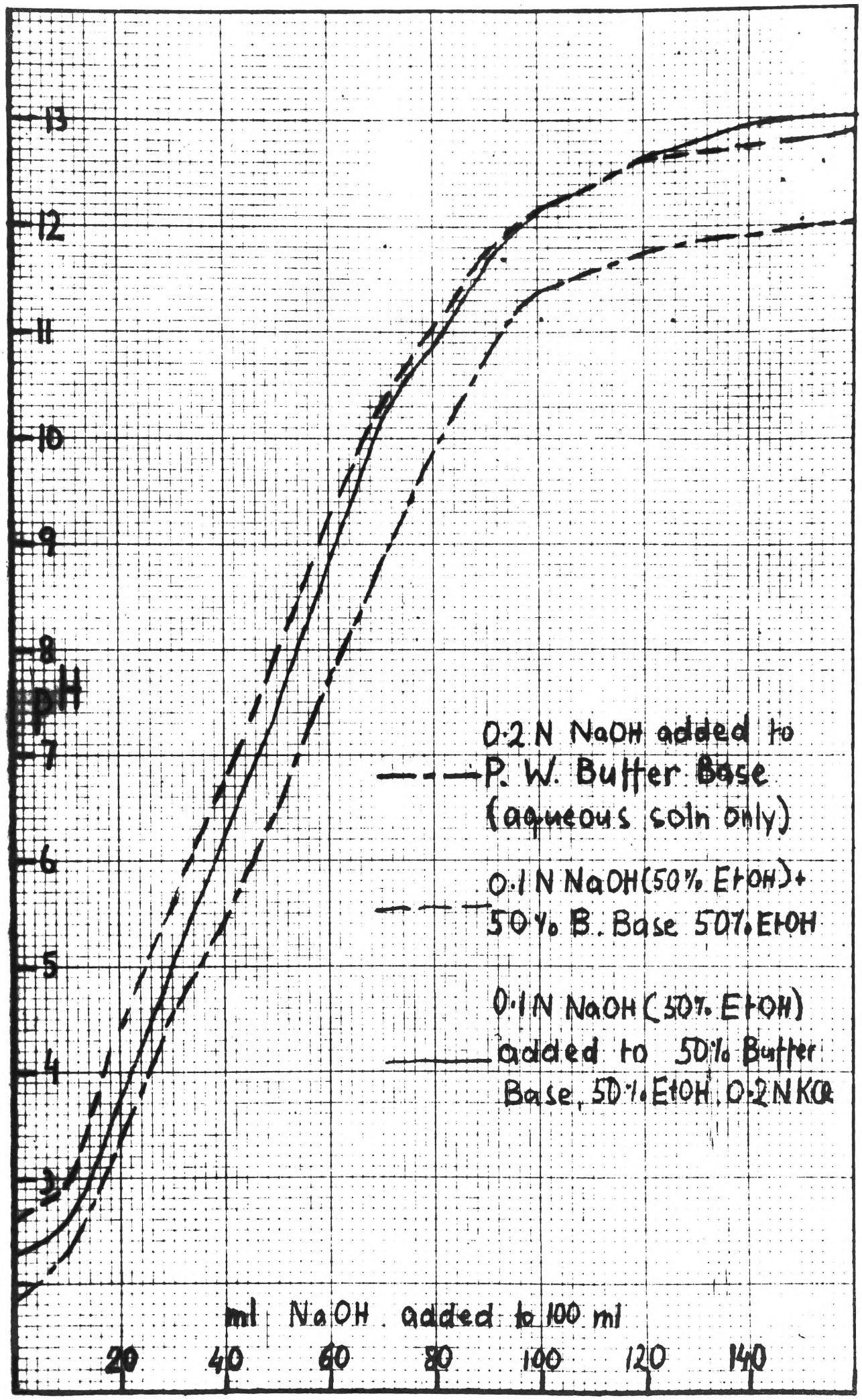


rcuit for Reduction at
Constant Potential



Polarographic Circuit

FIG. 6


pH
13
12
11
10
9
8
7
6
5
4
3
0.2 N NaOH added to P. W. Buffer Base (aqueous soln only)
0.1 N NaOH (50% EtOH) + 50% B. Base 50% EtOH
0.1 N NaOH (50% EtOH) added to 50% Buffer Base, 50% EtOH, 0.2 N KCl
ml NaOH added to 100 ml
20
40
60
80
100
120
140

distilled and stored for short periods in a dark bottle under nitrogen, when it became polarographically neutral. Most polarograms were produced at room temperature which ranged from 17-24°C.

A few polarograms are presented in figs. 7, 8 and 9, but the bulk of the polarographic results is given in tables 1 to 19. The difference between the potentials when $\frac{3}{4}$ and $\frac{1}{4}$ of the diffusion current are obtained is usually added to give an idea of the slope of the wave; it is 0.95 of the slope of the log $\frac{id-i}{i}$ curve between these points. The diffusion currents, i.e. current flowing at the plateaus minus current of supporting electrolyte at the same potential, will unless otherwise stated be given as $\frac{id}{kc}$ where c is expressed in millimoles per liter, id in microamps and k is the constant of the capillary used ($m^{2/3}\ t^{1/6}$). All half wave potentials are given against the saturated calomel electrode, and are, of course, negative, but the minus sign is omitted from the tables. Brief comments will be made at the foot of each table but the discussion of the results and derived curves will be left to the end of this section.

(b) Results:-

TABLE I.

PERINAPHTHENONE IN AQUEOUS BUFFERS, LEEDS AND NORTHRUP INSTRUMENT.

pH	c x 10^4	$E_{\frac{1}{2}}(1)$	$E_{\frac{1}{2}}(2)$	$E_{\frac{1}{2}}(3)$	$\frac{id(1)}{kc}$	$\frac{id(2)}{kc}$	$\frac{id(3)}{kc}$
1.8	1.50	.47	.90		2.5	1.9	
2.1	1.46	.55	1.00		2.3	2.3	
2.9	1.27	.59	.98		2.0	2.0	
5.1	1.11	.67	1.05		2.2	2.2	
6.0	1.05	.73	1.05	1.3	2.2	2.0	.1
7.0	1.00	.77	1.09	1.35	2.1	2.3	.3
8.0	.93	.82	1.12	1.35	2.0	1.9	.4
10.5	.87	.93	1.23		2.2	2.5	
11.6	.83	.95	1.32		2.2	2.5	
11.9	.81	.96	1.35		2.4	2.4	
12.3	.71	.97	1.39		2.5	2.5	

A nearly saturated solution of perinaphthenone was prepared by grinding excess solid in the aqueous buffer base solution, allowing it to stand for 2 days with frequent shaking and filtering it; [redacted] solutions of higher pH values were obtained by adding 0.2N NaOH to the previous sample. The concentration of the solution at pH 7 was obtained by comparison of its diffusion current with a solution of known concentration, obtained by dissolving 1.8 mg in 2 ml of alcohol and diluting it to 150 ml with a pH 7 buffer solution, the alcohol effect being neglected; concentrations of the other solutions were calculated from the amount of caustic soda added. The higher values of the diffusion current in the alkaline solution are probably due to evaporation losses caused by the [redacted] longer passage of nitrogen through them. The small third waves shown at pH 6, 7, 8 may well be carried over at higher pHs by merging with the second wave. The half wave potentials appear approx. 0.05 volts more negative than those obtained in the

manual instrument; this being due to the time lag of the recorder and the reason for not using this instrument in later work.

TABLE 2.

EFFECT OF DILUTION ON THE DIFFUSION CURRENT AND HALF WAVE POTENTIALS AT pH7, L + N INSTRUMENT.

c x 10^4	$E_{\frac{1}{2}}(1)$	$E_{\frac{1}{2}}(2)$	id(1)	id(2)	$\frac{id(1)}{kc}$	$\frac{id(2)}{kc}$
0.09	.82	1.00	0.04	0.05	2.2	2.6
0.17	.83	1.05	0.08	0.10	2.3	2.8
0.28	.80	1.04	0.13	0.15	2.3	2.6
0.45	.79	1.07	0.23	0.22	2.4	2.3
0.50	.80	1.07	0.24	0.26	2.3	2.5
0.67	.79	1.08	0.32	0.34	2.3	2.4
0.75	.79	1.09	0.35	0.39	2.3	2.5
0.81	.78	1.10	0.39	0.42	2.3	2.5
1.0	.76	1.08	0.41	0.53	2.2	2.5

TABLE 3.

PERINAPHTHENONE IN AQUEOUS BUFFERS, MANUAL INSTRUMENT.

pH	$E_{\frac{1}{2}}(1)$	$E_{\frac{1}{2}}(2)$	$E_{\frac{1}{2}}(3)$	id(1)	id(2)	id(3)	c x 10^4M approx.
0	0.27	0.67		0.6	0.3		1.0
1.0	0.33	0.78+0.88		0.5	0.4		1.0
2.1	0.42	0.93		0.6	0.7		1.3
2.9	0.47	0.74+0.97		0.8	0.8		1.8
3.9	0.55	0.98		0.7	0.6		1.4
5.1	0.60	1.00	1.30	0.6	0.6	0.1	1.3
6.0	0.66	1.03	1.32	0.5	0.5	0.1	1.1
7.0	0.71	1.05		0.5	0.6		1.1
8.0	0.77	1.08		0.5	0.6		1.1
10.5	0.84	1.15	1.4	0.5	0.5	0.2	1.1
11.6	0.90	1.32		0.4	0.5		0.9
11.9	0.91	1.34		0.4	0.7		0.9
12.3	0.92	1.34		0.4	0.4		0.9

+ The second wave showed a small prewave.

Individual buffer solutions were made up, stood over triturated Perinaphthenone for 2 days and filtered; the concentrations were estimated from the diffusion currents in the

same manner as in Table I. The solutions were diluted (with buffer) to $^{5}/_{6}$, $^{3}/_{4}$, $^{2}/_{3}$ and $^{1}/_{2}$ saturation and repolarographed. As their concentration is very low and the instrument was used at the maximum sensitivity no further dilution was possible. The diffusion currents on dilution were, within experimental error, proportional to concentration. There were no significant changes in the half wave potential of the first wave, but some of those of the second wave (in acid solutions) were shifted to more positive values on dilution, for instance at pH 3.9.

$E_{\frac{1}{2}}(2)$ =	1.00	0.98	0.95	0.92
conc.	std.	$^{5}/_{6}$ std.	$^{3}/_{4}$ std.	$^{1}/_{2}$ std.

TABLE 4.

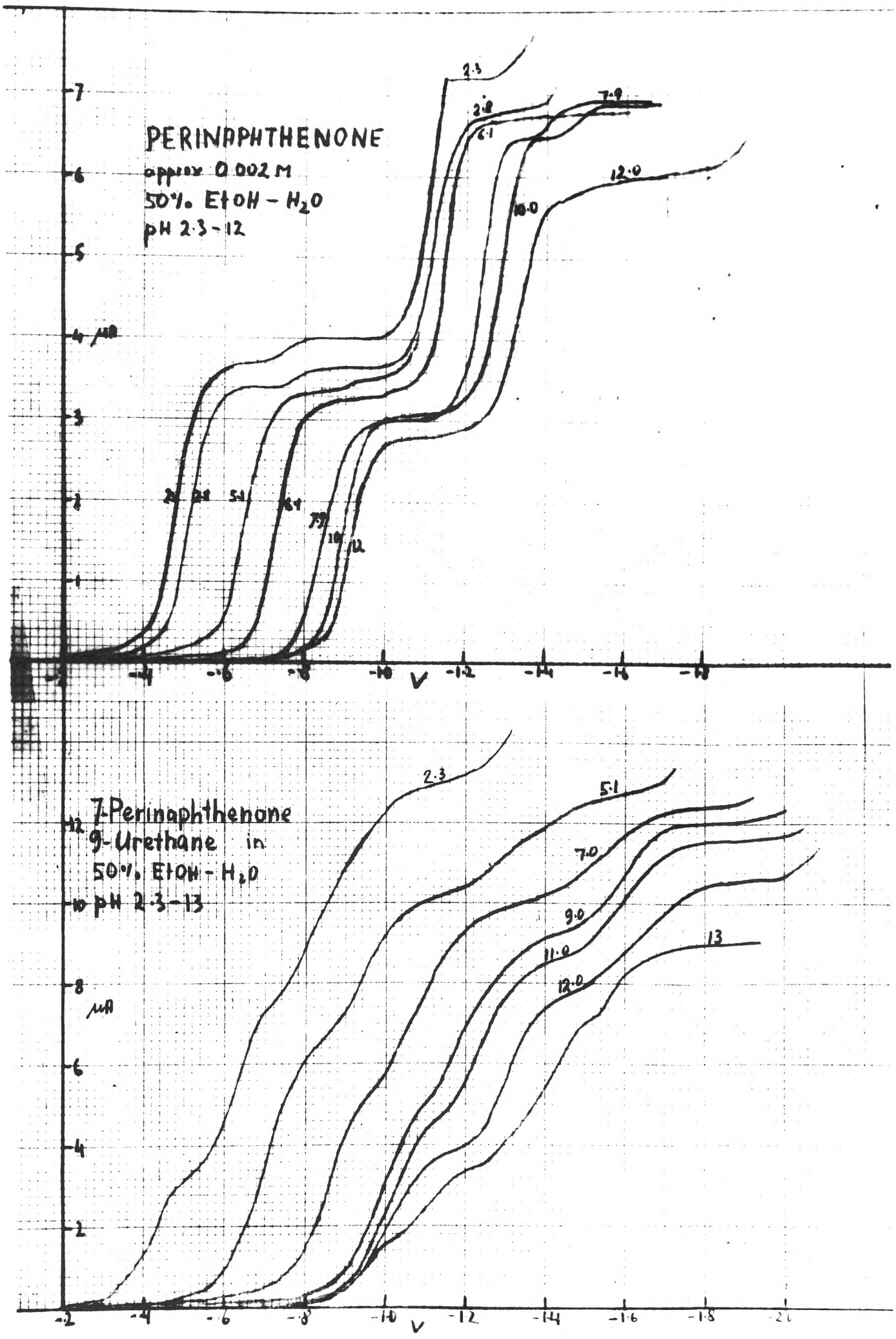
PERINAPHTHENONE IN 50% ETHANOL - WATER.

pH	10^3C	WAVE I. $E_{\frac{1}{2}}$	WAVE I. $E_{\frac{3}{4}}-E_{\frac{1}{4}}$	WAVE I. $\frac{id}{kc}$	PRE-WAVE 2. $E_{\frac{1}{2}}$	PRE-WAVE 2. $\frac{id}{kc}$
0.5	1.67	.37	.07	0.90	-	-
2.3	2.00	.47	.06	1.26	0.74	.12
2.8	1.82	.51	.06	1.27	0.78	.08
4.1	1.67	.59	.06	1.40	0.85	.08
5.1	1.54	.65	.05	1.38	0.90	.06
6.1	1.45	.73	.06	1.48	1.00	.02
7.0	1.37	.77	.06	1.52	1.06	tr
7.9	1.30	.84	.06	1.54	1.05	tr
9.0	1.26	.88	.05	1.60	1.09	tr
10.0	1.23	.89	.06	1.64	1.14	tr
11.0	1.19	.90	.05	1.64	-	-
12.0	1.11	.91	.05	1.63	-	-
13.0	1.67	.91	.06	1.35	-	-

	WAVE 2. $E_{\frac{1}{2}}$	WAVE 2. $E_{\frac{1}{2}}-E_{\frac{1}{4}}$	WAVE 2. $\frac{id}{kc}$	WAVE 3. $E_{\frac{1}{2}}$	WAVE 3. $\frac{id}{kc}$	id(1):id(2):id(3)
0.5	0.97	.03	0.86			1 : 0.96 : -
2.3	1.09	.03	1.10			1 : 0.97 : -
2.8	1.10	.03	1.19			1 : 1.00 : -
4.1	1.10	.02	1.36			1 : 1.03 : -
5.1	1.09	.02	1.51			1 : 1.14 : -
6.1	1.14	.02	1.62			1 : 1.17 : -
7.0	1.17	.03	1.84	1.33	0.10	1 : 1.20 : 0.06
7.9	1.22	.02	1.79	1.40	0.27	1 : 1.17 : 0.18
9.0	1.25	.03	1.90	1.44	0.23	1 : 1.18 : 0.14
10.0	1.27	.03	1.91	1.47	0.23	1 : 1.16 : 0.14
11.0	1.29	.04	1.91	1.49	0.18	1 : 1.16 : 0.11
12.0	1.32	.03	1.70	1.56	0.21	1 : 1.05 : 0.13
13.0	1.39	.03	1.41	1.63	0.10	1 : 1.05 : 0.07

With the exception of pH 0.5 and 13.0, which were made up separately, all determinations were carried out on the originally 0.002 molar solution of perinaphthenone in a 50% ethanol buffer base and 0.1N NaOH in 50% ethanol was added to it to increase the pH. This method is used for all series of polarograms showing the effect of pH. Although the nitrogen used for deaerating was bubbled through 50% ethanol it appears that some evaporation took place and therefore the values of $\frac{id}{c}$ will tend to be high for the higher pH

FIG. 7


PERINAPHTHENONE
approx 0.002 M
50% EtOH - H2O
pH 2.3 - 12
2.3
2.8
6.1
7.9
10.0
12.0
μA
V
7-Perinaphthenone
9-Urethane in
50% EtOH - H2O
pH 2.3 - 13
2.3
5.1
7.0
9.0
11.0
12.0
13
μA
V

values; dearation will have proceeded there for up to 8 hours. The second wave, particularly in acid medium, showed a tendency to give maxima and hence its shape is somewhat distorted; therefore $E_{\frac{1}{2}}-E_{\frac{1}{4}}$ is used, giving the slope of the lower half of the wave only. The second wave has its prewave incorporated in it in column 15 of Table 4 where the diffusion currents of waves 1, 2 and 3 are compared.

TABLE 5.

EFFECT OF DILUTION ON THE DIFFUSION CURRENT AND HALF WAVE POTENTIAL OF PERINAPHTHENONE IN 50% ETHANOL.

10^3c	$E_{\frac{1}{2}}(1)$	$E_{\frac{1}{2}}(2)$	id(1)	id(2p)	id(2) + id(2p)	$\frac{id(1)}{kc}$	$\frac{id(2)}{kc}$
			pH 2.8				
1.30	0.50	1.15	3.4	0.3	3.4	1.2	1.2
0.91	0.51	1.10	2.3	0.2	2.4	1.2	1.3
0.48	0.52	1.06	0.95	0.1	1.0	1.0	1.0
			pH 4.1				
1.67	0.60	1.12	3.15	0.15	2.85	1.3	1.2
0.91	0.60	1.08	1.7	0.1	1.6	1.3	1.2
0.41	0.60	1.08	0.7	0.1	0.7	1.2	1.2
			pH 10.2				
1.67	0.90	1.28	3.2		3.0	1.3	1.2
0.91	0.90	1.26	1.7		1.9	1.3	1.4
0.41	0.91	1.24	0.7		0.8	1.2	1.4
			0.1N NH_4 NO_3				
1.82	0.70	1.12	3.7		6.2	1.4	2.4
1.39	0.70	1.11	3.1		5.2	1.5	2.6
0.95	0.70	1.10	2.0		3.6	1.5	2.7
0.58	0.70	1.10	1.2		2.8	1.4	3.4
0.39	0.70	1.10	0.8		1.6	1.4	2.8
0.20	0.70	1.10	0.5		1.1	1.7	3.8

id(2p) is the height of the pre-wave occurring at 0.85V(SCE) at pH 2.8 and at -0.93V at pH 4.1; it is included in the total diffusion current wave 2 for easy comparison. At pH 10.2 the small third wave occurs but it is not shown

here. Polarograms in ammonium nitrate show neither pre- nor third waves but a greatly increased second wave.

TABLE 6.

PERINAPHTHENONE IN STRONG ACID.

No.	10^3c	WAVE I.			WAVE 2. PREWAVE		WAVE 2. MAIN WAVE		
		$E_{\frac{1}{2}}$	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$	$\frac{id}{kc}$	$E_{\frac{1}{2}}$	$\frac{id}{kc}$	$E_{\frac{1}{2}}$	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$	$\frac{id}{kc}$
1	5.0	0.26	.056	.87	.50	.05	0.70	.14	.53
2	2.0	0.26	.056	.87			0.70	indeterminate	
3	2.5	0.23	.062	.88	.57	.07	0.70	.17	.65

No.					WAVE 2. $E_{\frac{1}{2}}$	WAVE 2. $\frac{id}{kc}$	$E_d(H_2)$
4	10	0.18	.04	.30	.55	.02	.92
5	5	0.19	.03	.36	.55	.02	.90
6	2.5	0.20	.04	.53	.55	.02	.89
7	1.25	0.22	.05	.86			.85
8	.625	0.25	.06	.9			.83
	5N HCl only						.78

The solvent for Nos. 1 and 2 was 10% $HClO_4$ conc; for No. 3 10% H_2SO_4 in glac. Acetic acid, for No. 4 10N HCl and for Nos. 5-8 5N HCl. The potentials are not corrected for any junction potentials. E_dH_2 is the "deposition potential" of Hydrogen obtained by projecting the (arbitrary) line of the slope of 1 microamp. per volt of the Hydrogen evolution curve onto the plateau preceding it.

TABLE 7.

EFFECT OF MERCURY HEAD ON DIFFUSION CURRENT OF PERINAPHTHENONE.

h	t	$\frac{id(1)}{c}$	$\frac{id(2)}{c}$	$\frac{id(1)}{c\sqrt{\frac{h}{400}}}$	$\frac{id(2)}{c\sqrt{\frac{h}{400}}}$	$\frac{id(1)}{kc}$	$\frac{id(2)}{kc}$
200	6.4	1.85	1.50	2.8	2.1	1.3	1.0
300	4.3	2.40	2.45	2.75	2.8	1.3	1.3
400	3.2	2.85	2.80	2.85	2.8	1.4	1.3
500	2.3	3.10	3.00	2.75	2.55	1.3	1.3
600	1.9	3.25	3.10	2.65	2.55	1.2	1.2

h = head of mercury in millimeters
t = drop time in seconds at -0.7V(S.C.E.)
k = $m^{2/3} t^{1/6}$ is taken from standardization of capillary = 2.08 at 400 mm.

The second wave at 200 mm shows a sharp flattening which may well be due to adsorption of the product on the drop during its long lifetime.

TABLE 8.

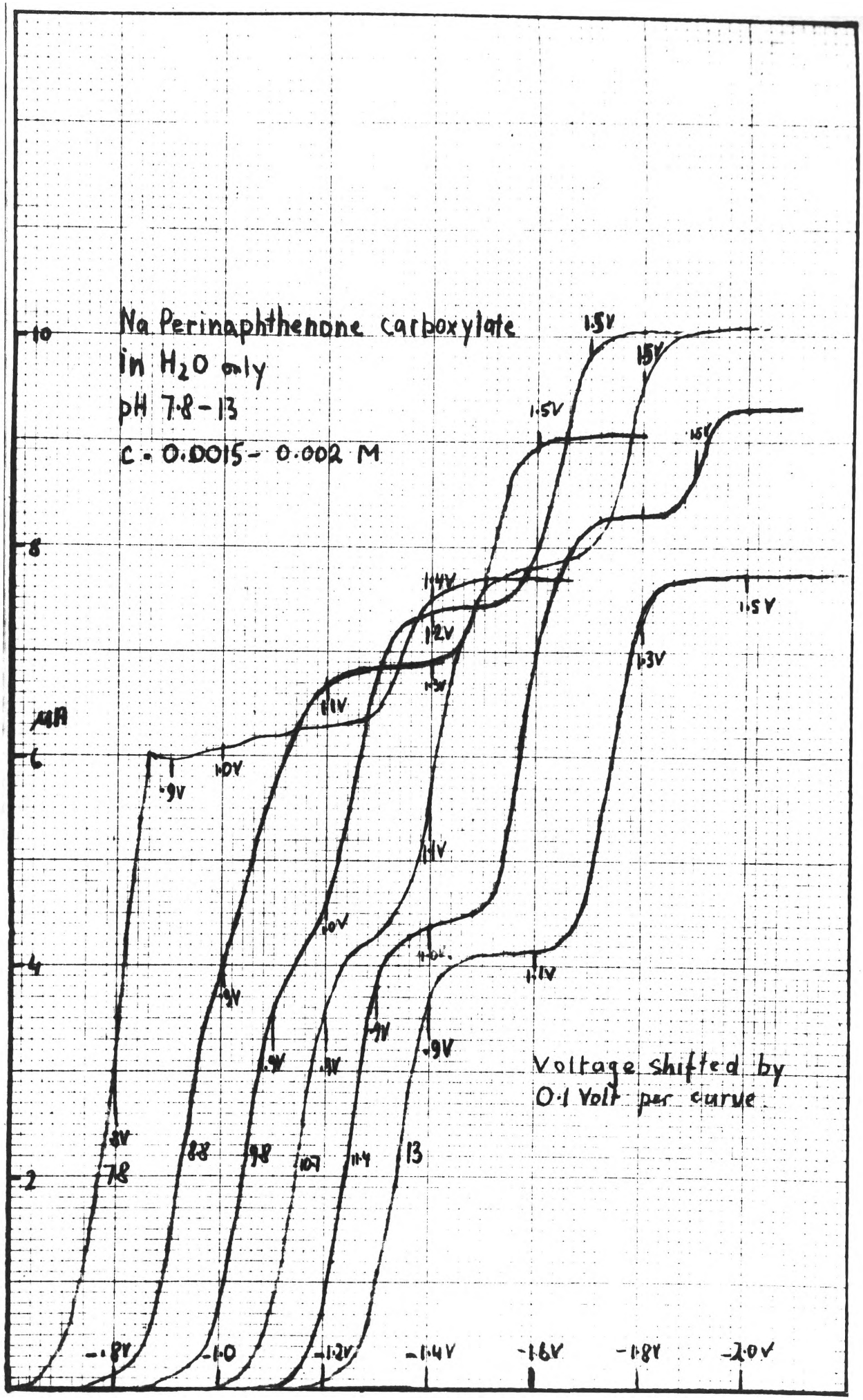
PERINAPHTHENONE CARBOXYLATE IN WATER.

		WAVE I.			WAVE 2.		
10^3c	pH	$E_{\frac{1}{2}}$	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$	$\frac{id}{kc}$	$E_{\frac{1}{2}}$	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$	$\frac{id}{kc}$
4	13	.84	.07	1.75	1.23	.06	1.54
2	11.4	.85	.06	1.88	1.175	.06	1.68
1.9	10.7	.845	.07	1.95	1.10	.07	1.55
1.77	9.8	.84	.07	2.00	1.05	.065	1.60
1.65	8.8	.81	.06	3.58	.96	.09	X
1.5	7.7	.74	.06	3.60	.82	.03	X

	WAVE 3.					
10^3c	$E_{\frac{1}{2}}$	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$	$\frac{id}{kc}$	id(1) :	id(2) :	id(3)
4	---	---	---	1.13 :	1 :	0
2	1.48	.05	.45	1.12 :	1 :	.27
1.9	1.46	.08	1.01	1.25 :	1 :	.65
1.77	1.44	.06	1.27	1.25 :	1 :	.78
1.65	1.40	.06	1.14		2 :	.65
1.5	1.34	.06	.80		2 :	.45

To a solution of perinaphthenone carboxylate in 0.1N NaOH aqueous buffer base was added. In more acid solutions

FIG. 8


Na Perinaphthenone carboxylate
in H_2O only
pH 7.8 - 13
c. 0.0015 - 0.002 M
μA
10
8
6
4
2
Voltage shifted by
0.1 Volt per curve
-0.8V
-1.0
-1.2V
-1.4V
-1.6V
-1.8V
-2.0V

precipitation occurred. At pH 7.7 and 8.8 the first and second waves are fused together; the values of $E_{\frac{1}{2}}$ therefore are actually $E_{\frac{1}{4}}$ and $E_{\frac{3}{4}}$ of the combined wave whilst $E_{\frac{3}{4}}-E_{\frac{1}{4}}$ show the slopes of the first and second half respectively. The combined wave at pH 7.7 shows a slight maximum and this may account for the steepness of its second half.

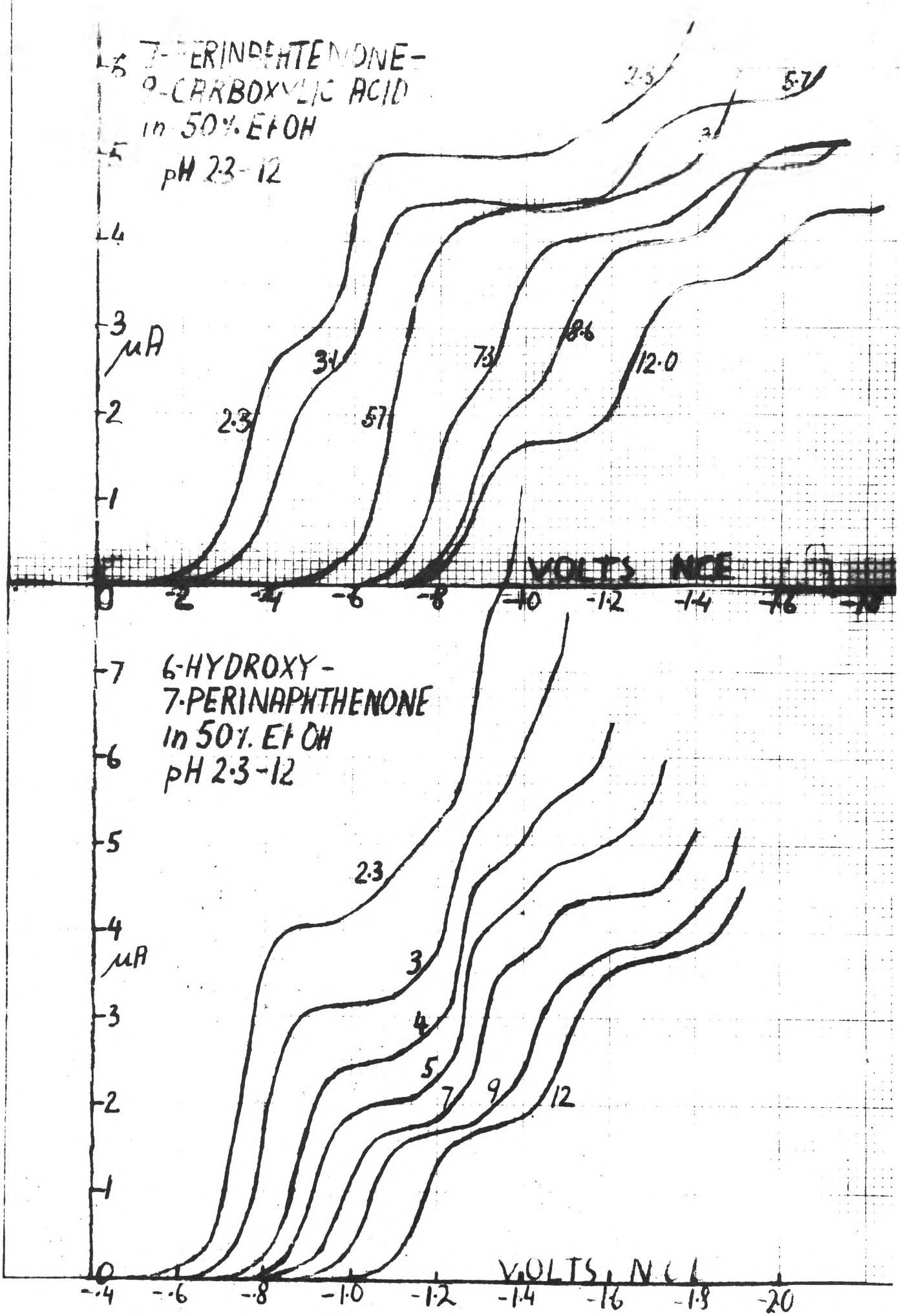
TABLE 9.

PERINAPHTHENONE CARBOXYLIC ACID IN 50% ETHANOL-WATER.

pH	10^3c	WAVE I. $E_{\frac{1}{2}}$	WAVE I. $E_{\frac{3}{4}}-E_{\frac{1}{4}}$	WAVE I. $\frac{id}{kc}$	WAVE 2. $E_{\frac{1}{2}}$	WAVE 2. $E_{\frac{3}{4}}-E_{\frac{1}{4}}$	WAVE 2. $\frac{id}{kc}$
0	0.85	.24	.06	.88	0.43	.02	1.0
1.0	1.16	.26	.08	1.10	0.48	.04	0.91
2.3	1.54	.34	.06	1.24	0.59	.06	1.04
2.6	1.44	.37	.07	1.24	0.61	.06	1.00
3.1	1.35	.42	.08	1.21	0.64	.06	0.92
4.3	1.27	.54	.07	1.27	0.68	.04	0.95
4.9	1.20	.62	.06	2.10	0.70	.05	X
5.7	1.14	.665	.05	2.55	0.75	.06	X
6.6	1.08	.75	.06	1.59	0.92	.07	0.91
7.3	1.03	.79	.06	1.40	0.96	.06	1.12
8.6	0.98	.87	.07	1.34	1.09	.08	1.26
10.2	0.94	.89	.06	1.26	1.19	.06	1.30
11.3	0.90	.89	.06	1.24	1.23	.07	1.31
12.0	0.83	.89	.06	1.24	1.24	.07	1.39
13.0	1.21	.89	.06	1.25	1.27	.07	1.30

pH	WAVE 3. $E_{\frac{1}{2}}$	WAVE 3. $E_{\frac{3}{4}}-E_{\frac{1}{4}}$	WAVE 3. $\frac{id}{kc}$	id(1) : id(2) : id(3)
0	0.86	.07	.5	0.88 : 1 : .5
1.0	0.95	.08	.5	1.20 : 1 : .55
2.3				1.20 : 1 : -
2.6				1.24 : 1 : -
3.1				1.32 : 1 : -
4.3	1.16	.08	.58	1.34 : 1 : .61
4.9	1.21	.09	.90	2 : .85
5.7	1.28	.06	.55	2 : .43
6.6	1.34	.075	.45	1.73 : 1 : .5
7.3	1.38	.075	.5	1.25 : 1 : .5
8.6	1.46	.07	.8	1.07 : 1 : .64
10.2	1.52	.05	.63	0.97 : 1 : .49
11.3	1.54	.08	.7	0.95 : 1 : .56
12.0	1.56	.085	.6	0.90 : 1 : .44
13.0	1.59	.12	.3	0.96 : 1 : .23

FIG. 9


7-PERINAPHTENONE-9-CARBOXYLIC ACID
in 50% EtOH
pH 2.3-12
2.3
5.7
3
3.4
5.7
7.3
8.6
12.0
μA
VOLTS NCE
6-HYDROXY-7-PERINAPHTHENONE
in 50% EtOH
pH 2.3-12
2.3
3
4
5
7
9
12
μA
VOLTS, NCE

The waves at pH 4.9 and 5.7 were completely fused together and therefore indistinguishable. $E_{\frac{1}{2}}$ 1 and 2 are therefore $E_{\frac{1}{4}}$ and $E_{\frac{3}{4}}$ of the combined wave. Similarly the values for $E_{\frac{3}{4}}-E_{\frac{1}{4}}$ are actually $E_{\frac{7}{8}}-E_{\frac{5}{8}}$ and $E_{\frac{3}{8}}-E_{\frac{1}{8}}$ of the combined wave. The diffusion current for the combined wave is given as id(1). Maxima were found in the second wave between pH 2.3 and 4.9; in these cases $E_{\frac{3}{4}}-E_{\frac{1}{4}}$ was obtained by doubling $E_{\frac{1}{2}}-E_{\frac{1}{4}}$.

In solutions between pH 1 and 4.9 there appears also to be a strong adsorption of the product of the second wave. The droptime increased and the second wave is distinctly smaller than the first.

TABLE 10.

EFFECT OF ETHANOL ON THE POLAROGRAMS OF PERINAPHTHENONE CARBOXYLATE ION IN AN 0.2N AQUEOUS NaOH SOLUTION.

EtOH %	10^3c	id(1)/kc	id(2)/kc	id(3)/kc	$E_{\frac{1}{2}}1$	$E_{\frac{1}{2}}2$	$E_{\frac{1}{2}}3$	id(1)/id1(H_2O)	id(2)/id2(H_2O)
0	4.0	1.74	1.54	-	.84	1.23	-	1	1
2	3.9	1.73	1.52	-	n.	d.	-	.995	.99
9	3.6	1.65	1.44	-	n.	d.	-	.95	.93
17	3.3	1.50	1.37	-	n.	d.	-	.86	.88
28	2.85	1.29	1.23	.06	.89	1.25	1.68	.74	.80
50	2.0	1.07	1.19	.23	.89	1.26	1.62	.63	.78
75	1.0	1.28	1.45	.50	.93	1.26	1.62	.73	.95

Small amounts of ethanol were added to the aqueous solution of perinaphthenone carboxylate. The concentrations were then calculated from the amount of alcohol added neglecting the decrease of volume during mixing. In the dilute alcohol solutions only the diffusion current at the plateaus was determined.

TABLE 11.

EFFECTS OF CONCENTRATION ON THE DIFFUSION CURRENT OF PERINAPHTHENONE CARBOXYLIC ACID.

10^3c	id(1)	id(2)	id(3)	$\frac{id(1)}{kd}$	$\frac{id(2)}{kd}$	$\frac{id(3)}{kc}$	id(1):id(2):id(3)
			pH = 12.	$m^{2/3}$	$t^{1/6}$	= 1.42, 50% EtOH.	
0.109	.15	.15	.10	0.95	0.95	.64	1 : 1 : .67
0.20	.25	.25	.15	0.88	0.88	.52	1 : 1 : .6
0.34	.45	.45	.25	1.07	1.07	.59	1 : 1 : .56
0.52	.70	.70	.35	0.95	0.95	.45	1 : 1 : .5
0.655	.90	.85	.40	0.95	0.90	.43	1.05: 1 : .47
			pH = 12.	$m^{2/3}$	$t^{1/6}$	= 1.84, 50% EtOH.	
0.085	.12	.18	.08	0.87	1.26	.54	.67: 1 : .45
0.154	.28	.32	.15	0.92	1.17	.56	.87: 1 : .47
0.36	.80	.82	.38	1.20	1.22	.56	.97: 1 : .465
			pH = 12.	$m^{2/3}$	$t^{1/6}$	= 2.08 50% EtOH.	
0.36	1.0	0.7	0.4	1.30	0.91	.53	1.4 : 1 : .57
0.80	1.5	1.4	0.9	0.91	0.87	.62	1.07: 1 : .64
1.14	2.5	2.4	1.4	1.06	1.01	.58	1.2 : 1 : .58
2.0	4.6	4.2	2.2	1.10	1.01	.53	1.1 : 1 : .52
4.0	9.5	8.8	4.4	1.25	1.06	.53	1.08: 1 : .5
			pH = 11.5	$m^{2/3}$	$t^{1/6}$	= 1.16 in H_2O	
0.40	1.0	0.9	0.35	2.15	1.95	.75	1.1 : 1 : .39
0.80	1.7	1.55	0.55	1.82	1.67	.60	1.09: 1 : .35
1.33	3.2	2.5	0.75	2.07	1.62	.49	1.26: 1 : .30
2.00	4.4	3.9	1.05	1.88	1.69	.45	1.13: 1 : .27

There was no significant change with concentration in the half wave potentials of the samples.

TABLE 12.

EFFECT OF MERCURY HEAD ON DIFFUSION CURRENT OF PERINAPHTHENONE CARBOXYLIC ACID.

pH = 12, c = 0.004 M, 50% Ethanol.

h	$\frac{id}{c}$			$\frac{id}{c\sqrt{\frac{h}{400}}}$			$\frac{id}{kc}$		
	1	2	3	1	2	3	1	2	3
200	1.56	1.36	.95	2.2	1.9	1.4	1.18	0.95	0.66
300	2.03	1.79	1.38	2.4	2.2	1.6	1.10	0.97	0.75
400	2.41	2.19	1.10	2.4	2.2	1.1	1.16	1.06	0.53
500	2.75	2.62	1.15	2.5	2.4	1.0	1.16	1.11	0.48
600	2.92	2.70	1.07	2.4	2.2	0.8	1.12	1.05	0.40

h = head of mercury in mm.

k = $m^{2/3} t^{1/6}$ values taken from standardisation of capillary (2.08 at 400 mm)

TABLE 13.

PERINAPHTHENONE CARBOXYLIC ACID IN STRONG ACID.

(90% acetic, 10% perchloric acid)

$10^3 c$	WAVE I.			WAVE 2.			WAVE 3.		
	$E_{\frac{1}{2}}$	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$	$\frac{id}{kc}$	$E_{\frac{1}{2}}$	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$	$\frac{id}{kc}$	$E_{\frac{1}{2}}$	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$	$\frac{id}{kc}$
4	0.11	.07	.96	.43	.06	1.12	.66	.05	.22
2	0.11	.06	.94	.38	.06	1.12	.53		.23
1	0.11	.06	.94	.28		2.3	fused with 2.		

TABLE 14.

6-HYDROXYPERINAPHTHENONE IN 50% ETHANOL-WATER.

pH	10^3C	WAVE I. $E_{\frac{1}{2}}$	WAVE I. $E_{\frac{3}{4}}-E_{\frac{1}{4}}$	WAVE I. $\frac{id}{kc}$	WAVE 2. $E_{\frac{1}{2}}$	WAVE 2. $E_{\frac{3}{4}}-E_{\frac{1}{4}}$	WAVE 2. $\frac{id}{kc}$
2.3	2.0	0.75	.055	1.40	1.12*	.11 *	o.47*
3.0	1.75	0.79	.06	1.25	1.25	.08	0.87
4.0	1.64	0.84	.06	1.12	1.25	.055	1.03
5.0	1.54	0.91	.06	0.86	1.26	.045	0.86
6.0	1.45	0.95	.06	0.88	1.28	.05	0.88
7.0	1.37	0.98	.06	0.87	1.30	.04	0.87
8.0	1.28	1.00	.06	0.90	1.32	.07	0.90
9.0	1.25	1.03	.06	0.90	1.42	.08	1.08
10.0	1.20	1.06	.06	0.94	1.46	.09	1.12
11.0	1.17	1.11	.06	1.07	1.48	.06	1.07
12.0	1.10	1.16	.06	1.08	1.49	.06	1.14
13.0	0.84	1.21	.06	1.01	1.49	.065	1.16

pH	WAVE 3. $E_{\frac{1}{2}}$	WAVE 3. $E_{\frac{3}{4}}-E_{\frac{1}{4}}$	WAVE 3. $\frac{id}{kc}$	id(1) : id(2) : id(3)
2.3	1.28*	.04*	.90*	1 : .34* : .64*
3.0	1.4	.07	.46	1 : .70 : .37
4.0	1.42	.10	.63	1 : .92 : .56
5.0	1.41	.10	.43	1 : 1 : .5
6.0	1.42	.09	.44	1 : 1 : .5
7.0	1.44	.06	.44	1 : 1 : .5
8.0	1.46	.07	.42	1 : 1 : .46
9.0	1.74	.08	.22	1 : 1.2 : .24
10.0	1.74	.07	.17	1 : 1.2 : .18
11.0	-	-		1 : 1 : -
12.0	-	-		1 : 1.06 : -
13.0	-	-		1 : 1.15 : -

The wave shown as Wave 2 at pH 2.3 is absorbed into the following one at higher pH values but distorts its lower section. Wave 3 at pH 2.3 is thus equivalent to Wave 2 at higher pH values; the third wave [redacted] is probably overshadowed by the Hydrogen evolution at pH 2.3. The fusion of the two waves accounts for the high value of $E_{\frac{3}{4}}-E_{\frac{1}{4}}$ of wave 2; the upper section being much steeper.

TABLE 15.

6-HYDROXYPERINAPHTHENONE IN STRONG ACIDS.

		WAVE I.			WAVE 2.		
	10^3C	$E_{\frac{1}{2}}$	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$	$\frac{id}{kc}$	$E_{\frac{1}{2}}$	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$	$\frac{id}{kc}$
1	2	0.51	0.07	.55	0.73	0.07	.27
2	2	0.56	0.10	.85	fused with H2		
3	2	0.58	0.09	.40	- - - - - - - -		

The solvents used were:-

(1) 5N HCl in 50% ethanol-water pH calc. -0.4

(2) 60% Acetic acid, 40% perchloric acid.

(3) 50% " " , 50% sulphuric acid.

TABLE 16.

7-PERINAPHTHENONE-9-URETHANE IN 50% ETHANOL-WATER.

		Wave I.			Wave 2.			Wave 3.		
pH	10^3C	$E_{\frac{1}{2}}$	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$	$\frac{id}{kc}$	$E_{\frac{1}{2}}$	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$	$\frac{id}{kc}$	$E_{\frac{1}{2}}$	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$	$\frac{id}{kc}$
0	1	(.22	.08	.36)	(.69	.06	.23)	H_2 evolution		
		(.47	.07	.82)	(.85	.06	.21)	-1.2v		
2.3	2	(.33	.10	.40)	.76	.12	.55	"		
		(.54	.075	.45)						
3.0	1.78	(.37	.085	.40)	.80	.12	.60	"		
		(.58	.07	.51)						
4.1	1.67	.60	.13	.86	.87	.10	.75	1.38	.10	.45
5.1	1.58	.69	.09	.86	.94	.12	.50	1.36	.12	.34
6.1	1.45	.79	.09	.87	1.05	.11	.68	1.50	.115	.32
7.0	1.37	.85	.08	.93	1.08	.12	.80	1.52	.16	.40
7.9	1.30	.92	.09	.85	1.14	.12	.82	1.54	.10	.33
9.0	1.25	.98	.10	.86	1.21	.14	.77	1.59	.11	.45
10.0	1.23	.99	.08	.87	1.22	.14	.82	1.59	.08	.43
11.0	1.19	1.00	.08	.84	1.24	.09	.77	1.59	.11	.57
12.0	1.11	1.00	.08	.76	1.30	.08	.79	1.61	1.6	.57
13.0	1.0	(.96	.07	.45)	1.38	.12	.84	1.56		.34
		(1.12	.07	.36)						

The first wave is assumed to be split in acid solutions (and at pH13) as the diffusion current at the end of the second wave is equivalent to a one electron reduction. The same applies to the second wave at pH 0. The waves are all rather flat and come close to merging.

TABLE 17.

BENZANTHRONE IN 50% ETHANOL WATER MIXTURE.

pH	10^3C		$E_{\frac{1}{2}}$	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$	id	$\frac{id}{kc}$
2.3	2		.61	.060	3.1	1.32
4.8	1.67		.76	.058	2.3	1.18
6.9	1.43		.89	.060	2.0	1.19
9.8	1.25		1.05	.060	1.8	1.21
12.0	1.11	(1)	1.12	.060	1.2	0.92
		(2)	1.4	?	0.3	0.23
13.0	0.9	(1)	1.12	.060	0.6	0.57
		(2)	1.45	.060	5.5	5.3

Only one wave was found in acid and neutral solutions; the second one, appearing at pH12, is very poorly defined; but is predominant at pH13.

TABLE 18.

ALKALI INSOLUBLE PRODUCT FROM SILVER CATHODE REDUCTION (MW260)* IN 50% ETHANOL-WATER.

		WAVE I.			WAVE 2.			COMBINED WAVES I & 2.
pH	10^3C	$E_{\frac{1}{2}}$	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$	$\frac{id}{kc}$	$E_{\frac{1}{2}}$	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$	$\frac{id}{kc}$	$\frac{id}{kc}$
2.3	2	.47	.07	.62	.61	.07	.31	.93
3.0	1.8	.52	.06	.62	.66	.08	.33	.95
4.1	1.67	.58	.07	.66	.74	.08	.32	.97
6.1	1.45	.70	.06	.70	.83	.07	.27	.96
7.9	1.3	.78	.08	.86		-	0	.86
10.0	1.23	.86	.06	.75		-	0	.75
12.0	1.11	.90	.07	.73		-	0	.73
13.0	0.75	.92	.07	.71		-	0	.71

	WAVE 3.			WAVE 4.			COMBINED WAVES 3 & 4.
pH	$E_{\frac{1}{2}}$	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$	$\frac{id}{kc}$	$E_{\frac{1}{2}}$	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$	$\frac{id}{kc}$	$\frac{id}{kc}$
2.3	1.06	.06	.40	1.21	.06	.31	.71
3.0	1.07	.06	.44	1.27	.06	.33	.77
4.1	1.07	.06	.42	1.30	.18	.44	.86
6.1	1.10	.07	.53	1.40	.12	.31	.84
7.9	1.13	.06	.65	1.36	.14	.29	.94
10.0	1.19	.06	.79	1.40	.12	.29	1.08
12.0	1.25	.06	.75	1.44	.08	.33	1.08
13.0	1.36	.10	1.01	Fused with 3			1.01

* by courtesy of Dr. Challen, Sydney.

The concentrations are taken on the basis of perinaphthenone-residues/l ie on MW 180, whereas MW found* from B.P. elevation = 260.; therefore concentration in g millimoles/l will be $\frac{180}{260}$ = 0.69 of values given and $\frac{id}{kc}$ = 1.45 times values given above.

TABLE 19.

ALKALI SOLUBLE PRODUCT FROM SILVER CATHODE REDUCTION (M.W.180.)* IN 50% ETHANOL-WATER.

		WAVE I.			WAVE 2.		
pH	10^3C	$E_{\frac{1}{2}}$	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$	$\frac{id}{kc}$	$E_{\frac{1}{2}}$	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$	$\frac{id}{kc}$
2.3	2	.71	.08	.88	1.27	.11	1.10
4.1	1.67	.83	.09	.87	1.33	.12	.75
5.1	1.54	.91	.09	.86	1.29	.12	.52
7.0	1.37	1.09	.07	.66	1.29	.12	.66
9.0	1.26	1.285	.10	1.30		-	
11.0	1.19	1.34	.08	1.26		-	
12.0	1.11	1.385	.07	1.28		-	
13.0	0.91	1.405	.06	.64	1.58	.07	.61

* Molecular weight determination by courtesy of Dr. Challen, Sydney.

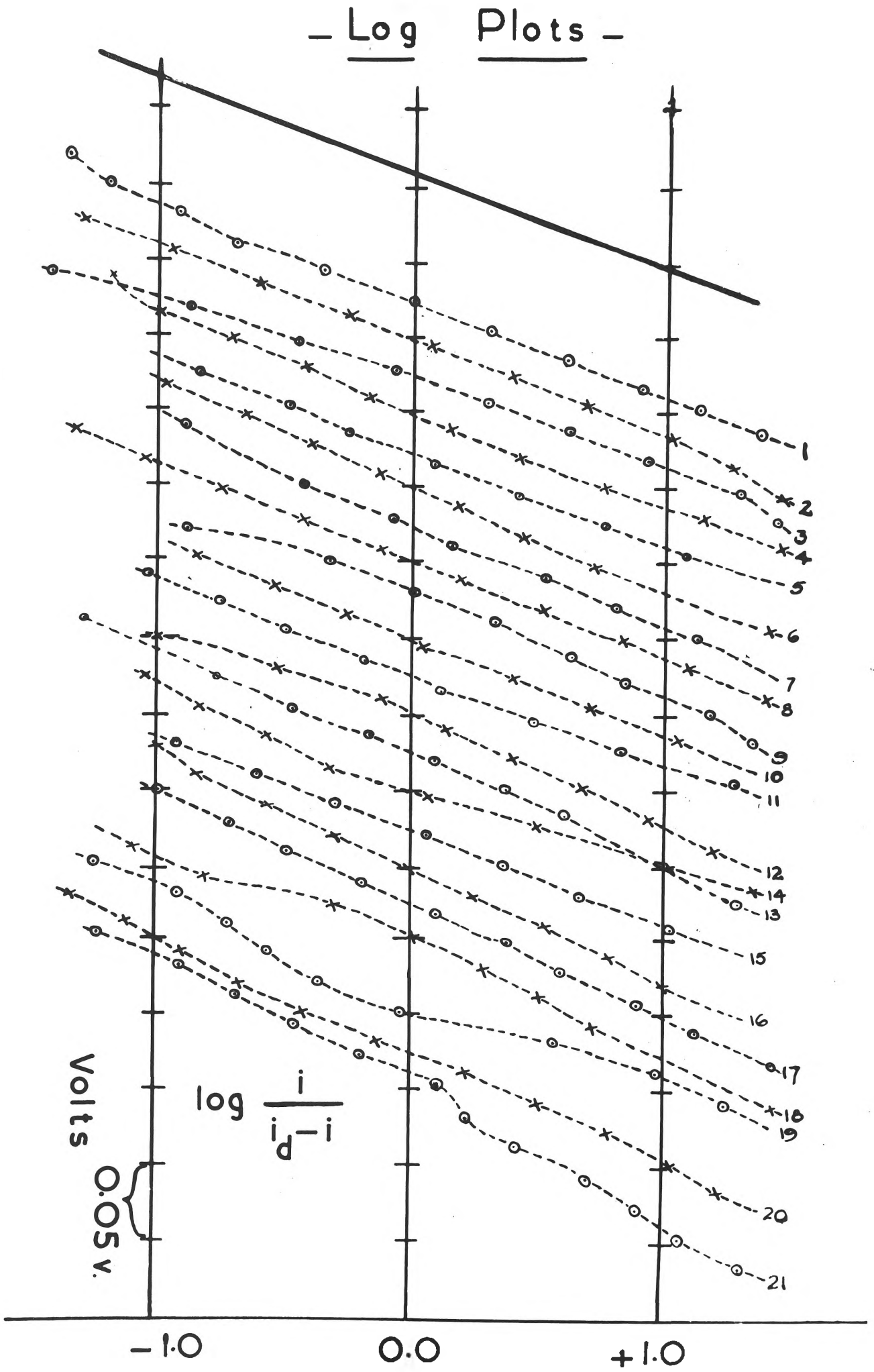
Fig. 10

$\log \frac{i}{id-i}$ against E.

No.	Wave	Substance	Solvent	pH	V Slope
1	1	perinaphthenone	50% EtOH	2.3	.060
2	1	"	"	7	.060
3	1	"	"	11	.055
4	1	perinaphthenone carboxylic acid	"	2.6	.063
5	1	"	"	12	.063
6	1	"	H_2O	10.7	.068
7	1	"	"	13.2	.065
8	1	hydroxy perinaphthenone	50% EtOH	2.3	.057
9	1	"	"	7	.064
10	1	"	"	12	.063
11	1	benzanthrone	"	2.3	.050
12	1	"	"	9.8	.061
13	2	perinaphthenone	"	2.3	.075
14	2	"	"	7	.048
15	2	"	"	11	.060
16	2	" carboxylic acid	"	11	.076
17	2	" "	H_2O	10.7	.076
18	2	" "	"	13.8	?
19	2	hydroxy perinaphthenone	50% EtOH	7	?
20	2	"	"	12	.070
21	3	perinaphthenone carboxylic acid	"	11	.085

The top line has the theoretical slope for a 1 electron reversible reduction, 0.06V.

FIG. 10


Log Plots
1
2
3
4
5
6
7
8
9
10
11
12
14
13
15
16
17
18
19
20
21
Volts
0.05 v.
log i / (i_d − i)
−1.0
0.0
+1.0

(c) Discussion

(i) Cathode Reactions -

The results obtained suggest that the polarographic reduction of perinaphthenone and its derivatives proceeds in three steps as illustrated in figures 11 and 12. The first is the formation of a free radical, the second one its reduction to an alcohol, enol or "naphthol", and the third one the reduction of a reformed ketone, most likely the naphthyl alkyl ketone formed by tautomerization of the enol (7 on fig.12). The reasons for these suggestions will be discussed below.

The first two waves are diffusion controlled ($id \propto c$) and $\left(\frac{id}{c} \propto \sqrt{h}\right)$ whereas the third one is at least partly rate controlled (tables 5, 7, 11 and 12). One electron only is involved in each of steps 1 and 2. This is distinctly shown by substituting the diffusion co-efficient (obtained from conductance measurements) of aqueous alkaline perinaphthenone carboxylate into the Ilkovic equation. The values of $\frac{id}{kc}$ (perinaphthenone average 1.3 in 50% Ethanol, 1.7 in water) also agree with those obtained by Pasternak (1) (Benzophenone in 60% alcohol 1.2 for 1 electron, 2.3 for 2 electrons), Geissman and Friess (88) (1.3 for chalcone in 50% isopropyl alcohol) and Day and Kirkland (96) (2.6 for benzophenone, 2.5 for anthrone and fluorenone for the combined step in 50% ethanol). The ratio $\frac{id\ (50\%\ EtOH)}{id\quad H_2O} = 0.70$ (Tables 8, 9, 10) agrees with that of Shreve and Markham (99) who found it to be 0.66 for nitro compounds.

The first wave of perinaphthenone is polarographically reversible. Reversibility of the reductions is indicated by

FIG. 11

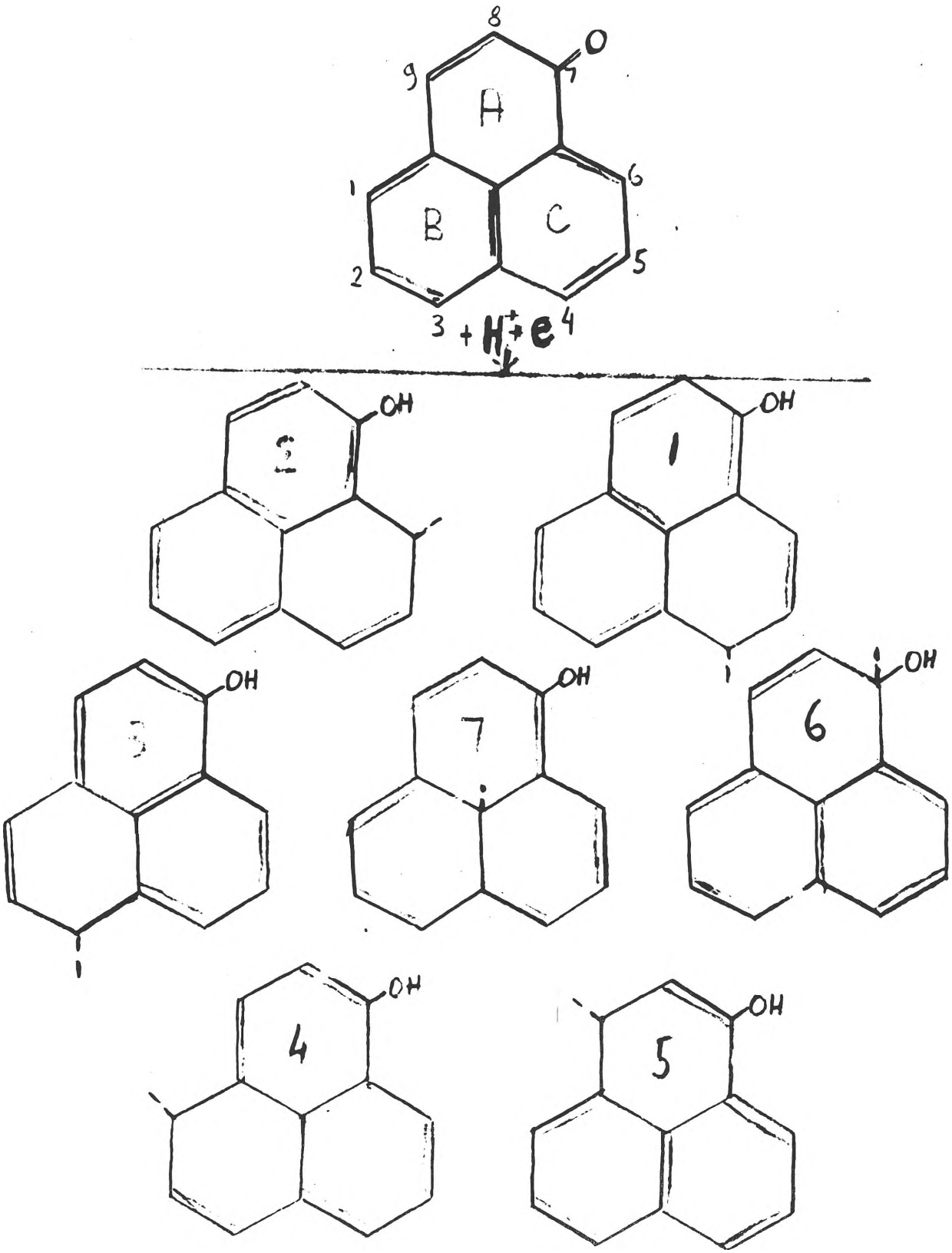
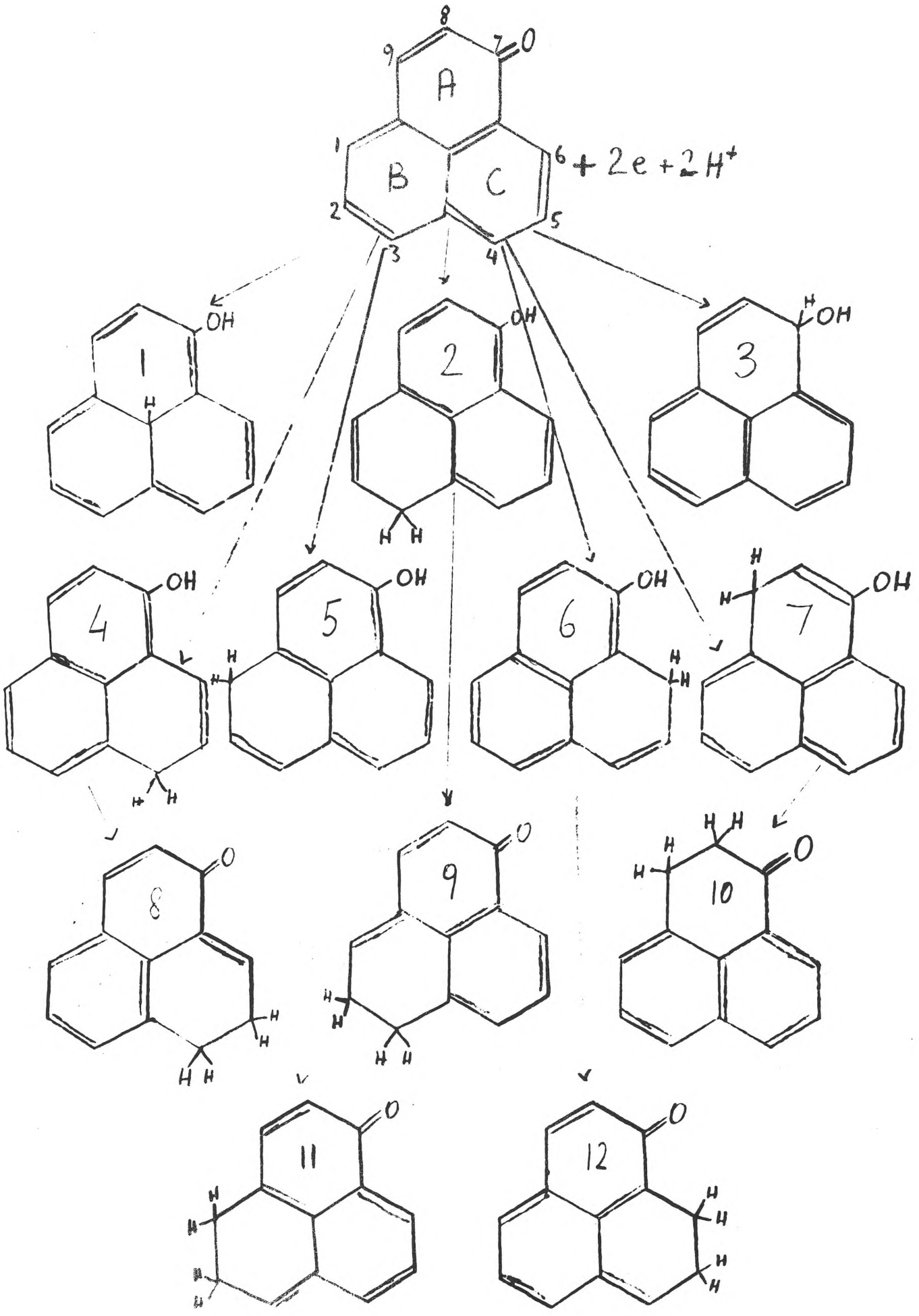


FIG. 12



the A.C. polarographic peak obtained by Bauer (100). The slope shows no appreciable steepening required for a fast bimolecular reaction (dimerization) competing with diffusion. (Note: graphs of log $\frac{i}{id-i}$ /E, fig.10). In alkaline conditions, where disproportionation is known to occur, the increase of the first wave at the expense of the second one is small. AC-DC Polarograms and the attainment of oxidation-reduction potentials of the expected value by a platinum electrode immersed into the solution during large scale reductions in alkaline media also prove this reversibly

The product of the first reduction step is a free radical indicated in fig. 11. Figs. 13 and 14 show the half wave potential to be pH dependent (0.06 V/pH) up to the pH of 9 indicating the reversible uptake of a Hydrogen ion; above pH 9 no Hydrogen is required as the enate ion is formed. Its estimated (from the break in the curve) Ka value is 1.6×10^{-9} which is of the order expected for vinyl naphthols.

The free radical will be reduced to the alcohols or "naphthols" shown in fig. 12 producing the second wave. The absence of the AC polarographic peak (100), the AC-DC polarogram (page 64) and the absence of any change in the oxidation-reduction potential of a solution being reduced at a potential equivalent to the secondwave, all indicate that this reduction is fully irreversible.

The third wave is always lower than the earlier ones and is rate controlled. Tautomerization of the enol to the

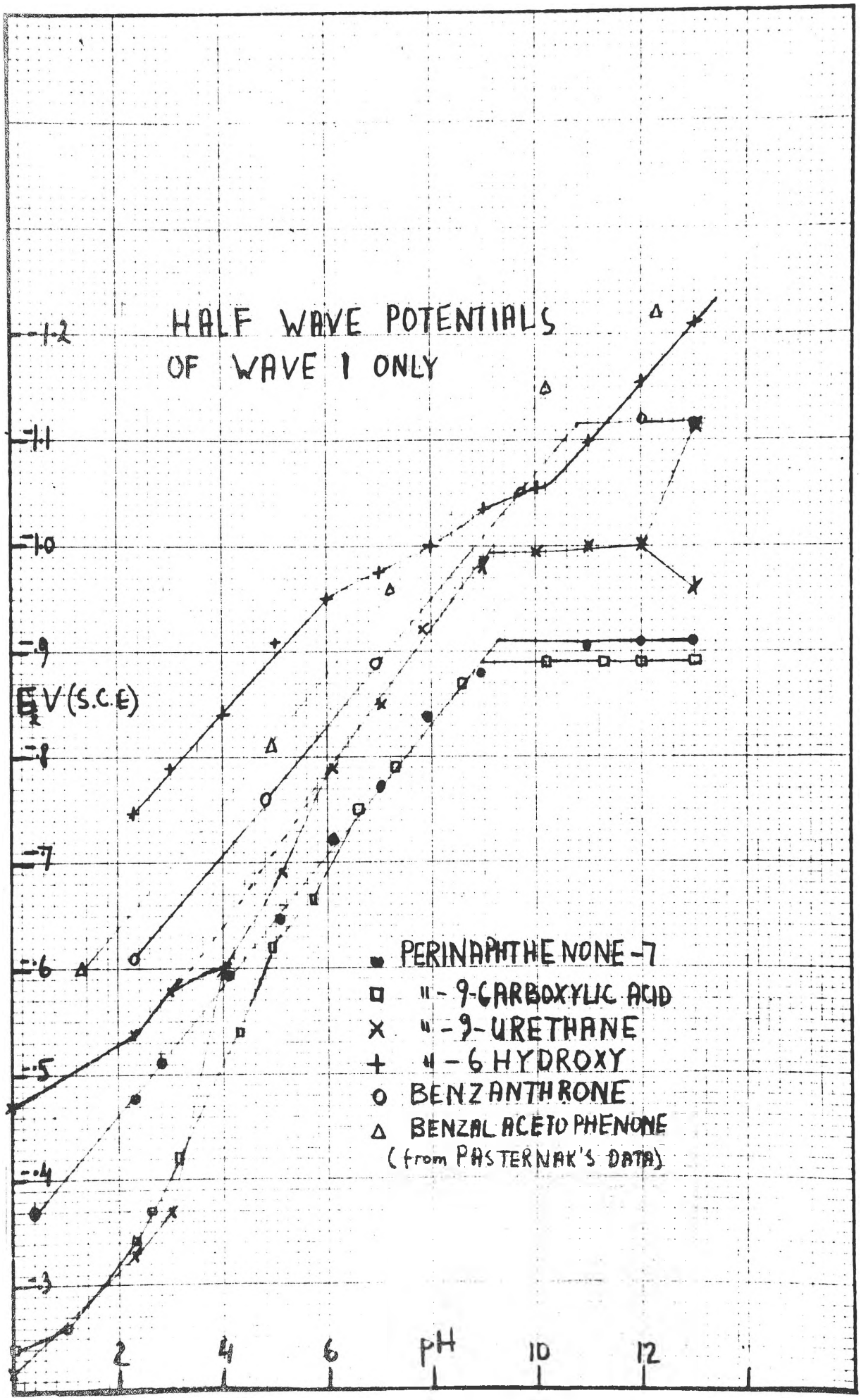
ketone is therefore relatively slow. It is also likely that only one of the reduction products (7 in fig.12) of the second step can ketonize in the available time.

(ii) Factors influencing the first step -

It will be noticed (fig.13) that the half wave potentials of the first waves follow the rules outlined earlier. Their position is determined mainly by the difference in free energy of reactant and product. Perinaphthenone will form the free radical without losing its aromaticity, the resonance energy (not counting the various possible positions of the unpaired electron) being increased since molecules containing α and β naphthol structures will be formed in addition to those containing the unsubstituted naphthalene ring (101). Its half wave potential is of the same order as that of Dibenzalacetone where the carbonyl group lies between 2 double bonds each conjugated to benzene rings. Benzanthrone will form a stable free radical containing the phenanthrol structure but this will occur at the expense of the resonance energies of the separate naphthalene and benzene rings in benzanthrone. Its reduction will therefore require a more negative potential than that of perinaphthenone.

The effect of electron donating and attracting groups is shown by the 9-carboxylic acid and the urethane. In acid solution the carboxylic group will withdraw electrons from the ring and thus make reduction easier; above a pH of 7 (when the carboxylate ion is present) this effect vanishes.

FIG. 13


HALF WAVE POTENTIALS
OF WAVE 1 ONLY
-1.2
-1.1
-1.0
-.9
-.8
-.7
-.6
-.5
-.4
-.3
$E_{\frac{1}{2}}$ V (S.C.E)
2
4
6
pH
10
12
PERINAPHTHENONE-7
" - 9-CARBOXYLIC ACID
" - 9-URETHANE
" - 6 HYDROXY
BENZANTHRONE
BENZALACETOPHENONE
(from PASTERNAK'S DATA)

In neutral conditions the urethane will act as an electron donating group thus making reduction more difficult. In acid and alkaline media its first wave is split, probably due to equilibria between urethane-keto and imide-enol forms.

The difficulty of reducing the 6-hydroxy-perinaphthenone-7 is due to the stabilization of the keto group by hydrogen bonding, which at the same time increases the electron density around carbon atom 7. The effect of the hydroxy group is much bigger in the 6-hydroxy-perinaphthenone-7 ($\Delta E_{\frac{1}{2}} = 0.25V$) than in 2-hydroxy-chalcone ($\Delta E_{\frac{1}{2}} = 0.04V$) (88), the keto and hydroxy groups being im similar neighbouring positions. The difference is due to the weaker hydrogen bonding in hydroxy-chalcone where the resonance stabilization of the hybrid of ketone + phenol and enol + quinone structures is less than that of the identical structures in the hydroxy-perinaphthenone. The difference in the case of protonation (pKa values of the conjugate acids, page 76) is small. The break in the $E_{\frac{1}{2}}$/pH curve between pH 6 and 10 must be due to the formation of the hydrogen bond stabilized ion $(\equiv C\text{-}O^{-}H\text{-}O\text{-}C \equiv)^{-}$ of somewhat lower energy content and requiring no proton. In more alkaline conditions the hydroxy group itself is ionized and a proton is again required to form the abovementioned ion. It is likely that extremely alkaline conditions would have to be reached before the second ionization of the di-hydroxy radical would take place.

The effect of alcohol on the half wave potentials of the first wave of perinaphthenone and its carboxylic acid is shown in fig. 14. Junction potentials should have no apparent effect since the same conditions applied when the pH of the alcoholic buffer solutions was determined; thus if the junction potential gives a higher apparent pH than the correct one, it would, at the same time, show a more negative half wave potential (0.06V/pH). Gardner (85) and Day, Millikan and Shults (97) obtained similar results; Gardner suggests that the increased ionic strength in water stabilizes the free radical; it seems more feasible that the activity coefficient of the ketone in a nearly saturated aqueous solution is decreased by alcohol more than that of the "naphthol" formed, since the reduction of the free radical proceeds easier in water than in alcohol.

(iii) Factors influencing the second step -

It was mentioned earlier that the half wave potential of the second wave occurred when the velocity of reduction of the free radical was equal to that of its removal from the electrode reaction layer. It is difficult to determine from the shape and position of the wave whether this is due to disproportionation, dimerization or diffusion. A shift to more negative potentials (producing further separation from the first wave) could therefore be due to increased stability of the free radical towards reduction or its decreased stability towards dimerization and disproportionation. Fast disproportionation would increase the height of the first wave at the expense of

the second one. Fast dimerization would show a steeper wave and a shift of the cross-over potential of AC-DC polarograms from the centre at lower frequencies. Since neither of these effects were found to any significant extent, it is assumed that the reduction of the free radical is opposed predominantly by its diffusion .

It appears that (fig.14) in the case of perinaphthenone the hydrogen ion concentration has only a small effect on the reducibility of the free radical indicating that the taking up of the electron only is the rate determining step, (Gardner (85) obtained similar results for the second step of Benzophenone). The presence of alcohol appears to slow down the reduction (except in strongly alkaline conditions). I n acid solutions the second wave shows a small prewave which disappears in more concentrated solutions. This is probably due to adsorption of the second reduction product similar to that found by Voriskova in pyocyanine (60). This adsorption in acid solution may also produce the proneness to form maxima of the second wave and was also detected during the AC polarographic investigation by Bauer (100).

The reduction of the free radical of the carboxylic acid proceeds at a more positive potential than that of perinaphthenone and is pH dependent (approx. 0.08V/pH);

FIG. 14

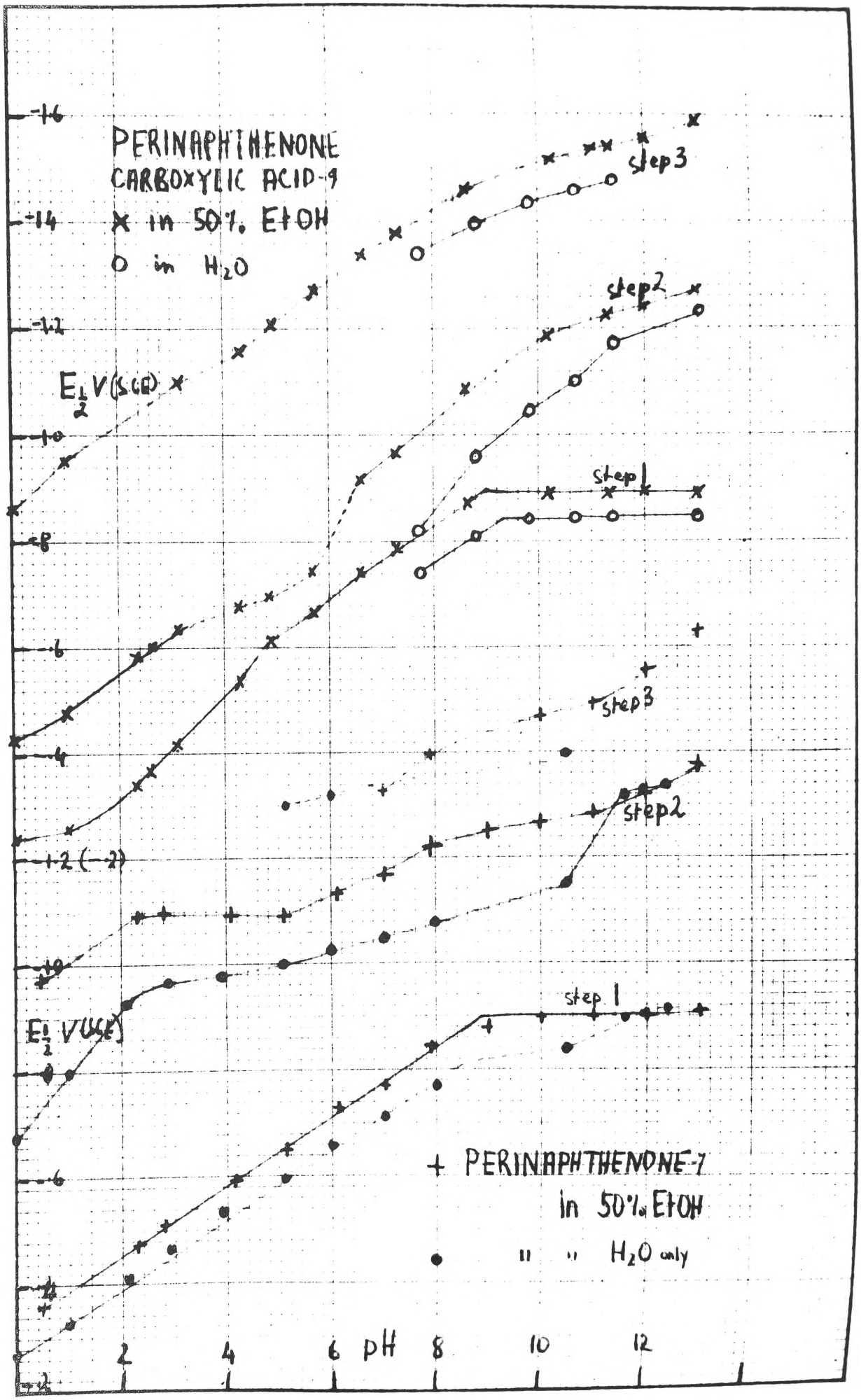
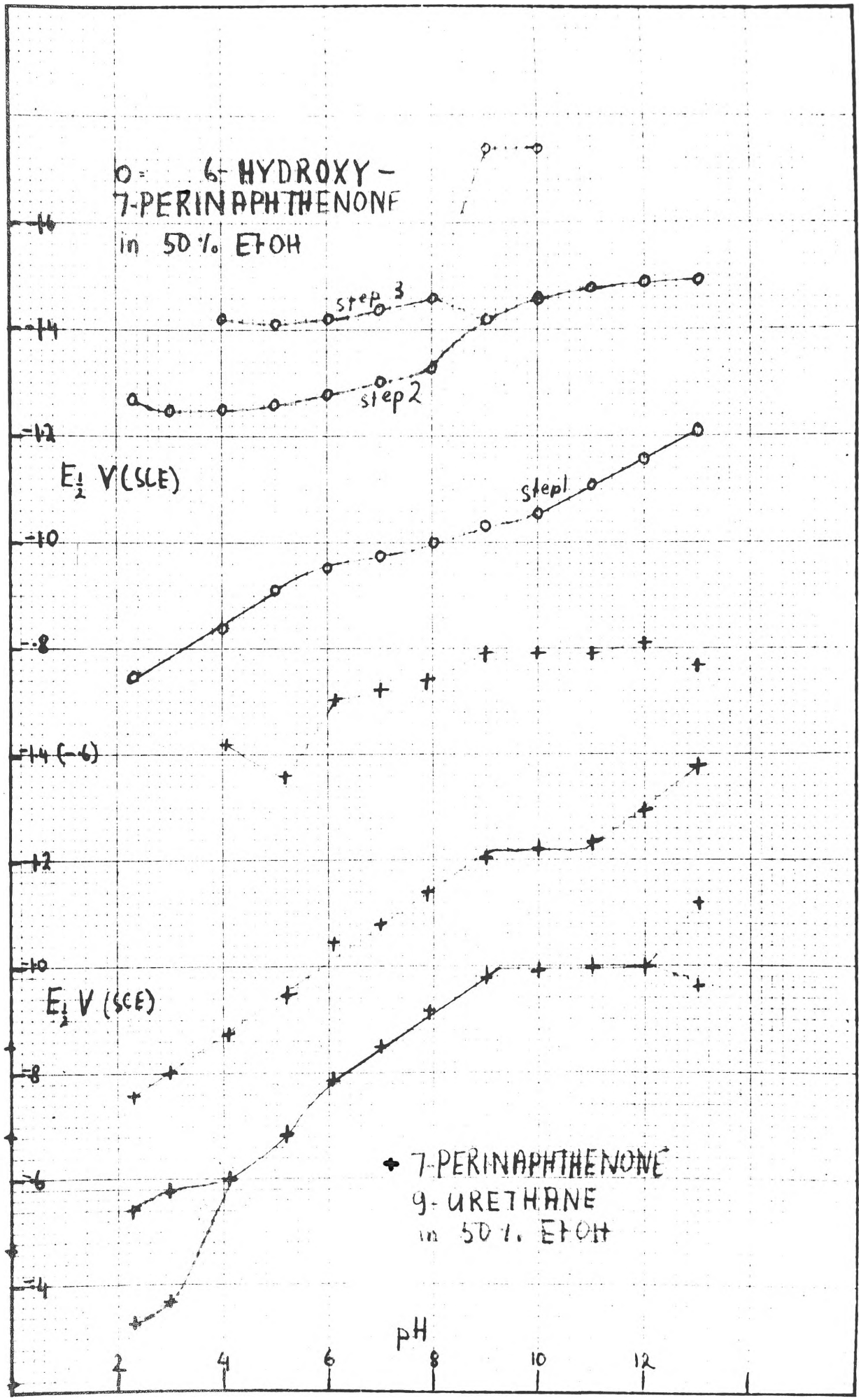

PERINAPHTHENONE
CARBOXYLIC ACID-9
× in 50% EtOH
○ in H2O
step 3
step 2
step 1
E½ V(SCE)
+ PERINAPHTHENONE-7
in 50% EtOH
" " H2O only
pH
2
4
6
8
10
12

FIG. 15


o - 6-HYDROXY-
7-PERINAPHTHENONE
in 50% EtOH
step 3
step 2
step 1
$E_{\frac{1}{2}}$ V (SCE)
-16
-14
-12
-10
-8
-14 (-6)
-12
-10
-8
-6
-4
+ 7-PERINAPHTHENONE
9-URETHANE
in 50% EtOH
pH
2
4
6
8
10
12

apparently the addition of the hydrogen ion is simultaneous to that of the electron. It is sufficiently fast in the pH range of 4-6 at the reduction potential of the first wave (which rises very quickly just below this pH range due to the neutralization of the carboxylic acid) to merge with it, producing combined waves of the type suggested by Delahay (62) (shown in fig. 4). Its ease of reduction may well be due to the increased localisation of the free electron at carbon atom 9 from where it will be "dispersable" amongst three double bonds compared to two in any other position. This is also likely from the point of view of formation of the third wave. As in the case of perinaphthenone the reduction of the free radical appears to be slowed down by the addition of alcohol.

The free radical formed from 1-hydroxy-perinaphthenone-7 appears to be reduced at two different potentials; the second step is, especially in acid solutions, made up of 2 separate waves. (fig. 8). The first one (ill defined and not quoted separately in table 14 and fig. 15) appears at a potential similar to that of the second perinaphthenone step whereas the main one requires a more negative value. It is suggested that resonance between the forms carrying the unpaired electron in ring B (a 1, 8, dihydroxynaphthalene) and those carrying it in rings A or C (naphthols) is not continuous, i.e. involves a difference of energy levels, similar to the proposition by Clar (5, page 432) in respect to the perinaphthyl radical in

strongly acidic media. The "naphthol" forms should be of similar stability to the free radical formed by perinaphthenone, whereas the dihydroxy-naphthalene forms will possess the extra resonance stabilization due to another hydroxy group linked to the aromatic ring (101) making further reduction more difficult. Under more alkaline conditions this effect disappears and the extra stabilization due to hydrogen bonding mentioned earlier becomes apparent.

(iv) Factors influencing the third step -

The third wave is formed by the reduction of the products of the second step. It is therefore different from that obtained by Ashworth (84) with Benzophenone and Fluorenone where the second step of the reduction proceeds along two alternate paths. Since it is rate controlled and smaller than the second wave it is likely that the product of the second step has to rearrange. As will be seen from fig. 12, there are several different structural forms possible for this product. Structure 1 is unlikely due to the strained carbon-hydrogen bond in the centre; the saturated alcohol 3cannot rearrange. This leaves tne naphthol containing structures (2, 4, 5, 6) and the enol (7) as the possible precursors of the molecule producing the third step. The "naphthols" on rearrangement(which is likely to be slow)would produce unsaturated aromatic ketones which would be reduced in the vicinity of the second wave ($E_{\frac{1}{2}}$ of Ethylidenacetophenone at pH 11.3 is 1.28V(1)) which therefore

would be increased. Since this occurs only after large scale reductions (and when using ammonium nitrate) it appears to proceed only slowly.

The third step appears to be produced by the reduction of a naphthylalkylketone (10, fig 12) formed by tautomerization of the enol (7, fig 12). Its usual position is that to be expected since naphthylmethylketone has a half wave potential in tetramethyl ammonium hydroxide of 1.65V and in ammonium chloride of 1.42V (76). Its height will depend both on the rate of ketonization and the proportion of the enol (7), Fig 12 formed during the second reduction step.

In perinaphthenone only a small third wave appears. The 9-carboxylic acid gives a considerable wave which is decreased by strong alkali; alcohol will oppose this decrease (Tables 8, 9, 10, 11). It appears that the partial localisation of the free electron in position 9 mentioned earlier produces a bigger amount of the enol. High alkali (and low alcohol) concentration will stabilise the enate ion; under these conditions ketonization will be difficult. (The dissociation constant of all organic acids is lower in alcohol than in water (102)).

The "peri" dihydroxy compound formed by the addition of two hydrogens to the 9-hydroxyperinaphthenone will ketonize easily since the ketone is stabilized by hydrogen bonding; it is therefore also less reactive and the third

step occurs only at a more negative potential. As the pH increases and one of the hydroxy groups ionizes they are already linked by hydrogen bonding as mentioned earlier and their ketonization will become exceedingly difficult giving only a very small third wave, if any at all. 2'-hydroxychalcone, where a weaker hydrogen bond occurs also shows a decrease of the third wave with increased pH in the pH range of 6-9 (88).

Since the urethane can be considered to tautomerise between C-NH-C(OC_2H_5) = O and C-N = C(OC_2H_5) - OH an argument similar to that of the carboxylic acid in respect of the localised free electron can be applied.

(v) Polarography in Strong Acids -

In acetic acid - perchloric acid mixtures the first waves of the oxonium ions of perinaphthenone, and its hydroxy and carboxylic acid derivatives are all of approximately the same height ($\frac{id}{kc} \simeq .9$ compared to $\simeq 1.2$ in 50% ethanol) and their half-wave potential has been shifted by approx. .2V (.21 for perinaphthenone, .19 for the hydroxy, .23 for the carboxylic acid derivative) from that at pH 2.3 (Tables 6, 13, 15). It appears from these values that the reduction to the free radical still proceeds in the usual way.

The second waves vary, that of perinaphthenone being very drawn out, that of the carboxylic acid generally unchanged and that of the hydroxy derivative very small.

In strong hydrochloric acid adsorption of the free radical produced by the reduction of perinaphthenone appears to take place (Table 6). The adsorbed particles block the electrode surface so preventing further reduction and producing small values of the diffusion current at higher concentrations. They also make the evolution of hydrogen more difficult as shown by the small but definite shift in its "deposition potential."

(vi) Polarography of Benzanthrone -

Benzanthrone gives only a one electron step which is pH dependant. The free radical formed is sufficiently stable to diffuse from the electrode surface and its reduction is apparently too slow at potentials below the hydrogen evolution to compete with its diffusion. This may be expected since the free radical is formed by reduction with Sodium hydrosulphite or Zinc and hydrochloric acids and is chemically quite stable (23), (7). In strongly alkaline solutions Ring C is attacked by hydroxy ions (5 page 385). This form is then apparently reduced (four electrons being required) at a more negative potential than benzanthrone to the trimethylenephenanthrol with a fully saturated Ring C which is the usual chemical reduction product in alkaline conditions.

(3) DETERMINATION OF THE NUMBER OF ELECTRONS INVOLVED PER STEP.

The Ilkovic equation (page 13) shows that the diffusion current is dependent on the diffusion coefficient of the reducible particle and the number of electrons involved in the reduction. Since the diffusion coefficient of ions is also related to the ionic conductance the conductivities of solutions of sodium perinaphthenone carboxylate were determined.

50 mg of perinaphthenone carboxylic acid (0.22 millimoles) were triturated with 2.00 ml of 0.100N NaOH solution freshly made up from conductivity water. The solution was filtered and made up to 5 ml. This gave a 0.04M solution of the sodium salt (pH 6.9 glass electrode) which was the basis for the conductance measurements at 25°C shown below.

The ionic conductance for the perinaphthenone carboxylate ion was found to be 22 r.o.,(compared to 32.3 for the benzoate and 41 for the acetate ions)and the value of the diffusion coefficient obtained from it using the method of Kolthoff and Lingane is 5.9×10^{-6} $cm^2/sec.$ (compared to Pb^{++} $9.8 \times 10^{-6} cm^2/sec.$)

The number of electrons involved in the first wave were calculated by substituting the diffusion coefficient in the Ilkovic equation or by comparing the diffusion currents of Lead and Perinaphthenone carboxylate at the same temperature with their diffusion coefficients. The values obtained range from 1.0 to 1.2 showing clearly a one electron step. The conductance determinations and a sample calculation are shown in the appendix 2.

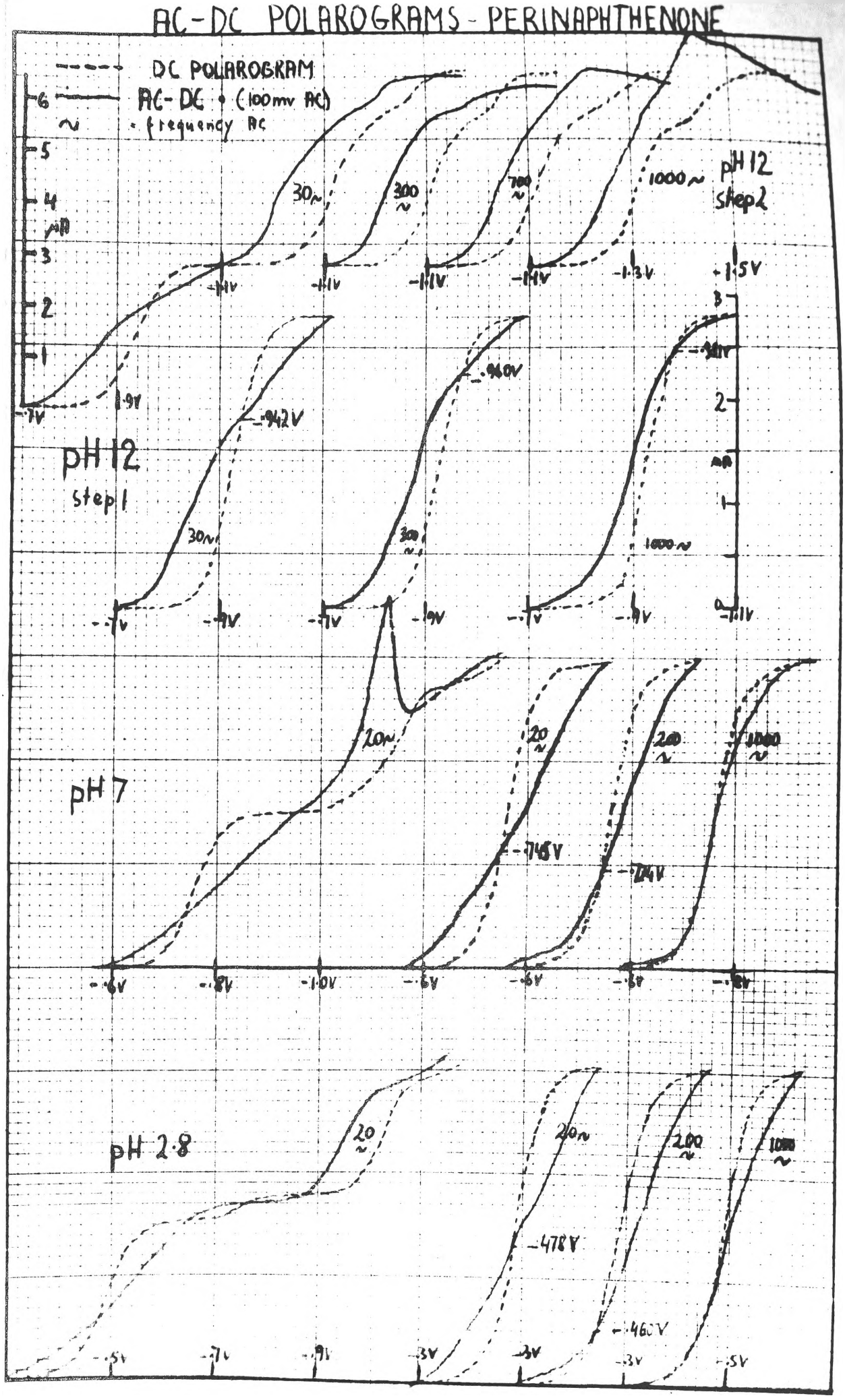
(4) A.C. - D.C. POLAROGRAPHY.

A.C.-D.C. polarograms of 0.001 M perinaphthenone in 50% ethanol-water buffers at pH 2.8, 7, and 12 were produced in collaborationwith Mr. Buchanan (N.S.W. U. of T, Sydney) on his equipment (69). The results are shown in fig. 16. Table 20 shows the shift in the steady applied potential. This shift is necessary to produce the same direct cell current when an alternating voltage of 100 millivolts is superimposed on the potential applied. The + sign indicates a shift to a less negative potential (in volts). The total diffusion current (first wave only) is 2.8 microamps at pH12, 3.0 microamps at pH7 and 3.05 microamps at pH2.8.

TABLE 20.

	pH 2.8			pH 7			pH 12		
$i_{\mu A}$	20~	200~	1000~	20~	200~	1000~	30~	300~	1000~
.1	+.6	+.4	0	+.7	+.4	+.1	+.9	+.8	+.8
.3	+.6	+.2	0	+.65	+.15	0	+.9	+.85	+.7
.5	+.55	0	0	+.5	+.1	0	+.8	+.7	+.6
.7	+.4	-.1	0	+.4	0	0	+.7	+.6	+.5
.9	+.3	-.2	0	+.25	-.1	0	+.6	+.5	+.4
1.1	+.2	-.25	0	+.05	-.2	0	+.55	+.4	+.3
1.3	0	-.3	-.05	-.05	-.25	0	+.5	+.4	+.3
1.5	-.2	-.35	-.1	-.2	-.3	0	+.35	+.4	+.25
1.7	-.4	-.4	-.15	-.45	-.4	-.05	+.2	+.4	+.25
1.9	-.5	-.4	-.2	-.5	-.45	-.1	-.1	+.3	+.2
2.1	-.55	-.45	-.25	-.6	-.45	-.15	-.3	+.2	+.2
2.3	-.6	-.45	-.3	-.7	-.5	-.2	-.35	0	+.15
2.5	-.65	-.5	-.35	-.75	-.6	-.3	-.45	-.2	+.05
2.7	-.65	-.6	-.4	-.8	-.6	-.3	-.7	-.4	-.05
2.8							-.7	-.4	-.2
2.9	-.6	-.5	-.4	-.75	-.4	-.3	0	0	0
3.0	-.4	-.3	-.2	0	0	0			
3.05	0	0	0						

FIG. 16


AC-DC POLAROGRAMS - PERINAPHTHENONE
DC POLAROGRAM
AC-DC • (100mv AC)
• frequency AC
pH 12
step 2
pH 12
step 1
pH 7
pH 2·8

The A.C.-D.C. Polarograms show a "partial" reversibility of the first and [redacted] irreversibility of the second wave. Since the "cross-over potential" of the first wave shifts away from the half wave potential with increased frequency, the "reversibility defect" cannot be due to the removal of the initial reduction product by a secondary reaction. This would have the opposite effect (69). It is suggested as possible that different "critical reaction velocities" of the oxidation and reduction processes or adsorption of the reduced and unreduced forms cause these shifts.

The effect of the superimposed alternating voltage appears to decrease at higher frequencies due to the inability of the electrode reaction to proceed at that speed (69). If this limiting velocity is higherfor one reaction, then the effect of increased frequency on its rectifying power will be less.(70) The cross over potential (at which both reactions cause equal rectification) will then shift towards positions of higher concentration of the other (slower) reagent.

Since the shift of the cross-over potential is towards more positive values with higher frequencyes at pH 2.8 and 7 (Table 20, fig. 16) it appears that the "critical velocity" of the reduction process is less than that of the oxidation process. The opposite applies at pH 12. This seems reasonable as the reduction process in acid and neutral media involves the addition of an electron and hydrogen ion to perinaphthenone whereas under alkaline conditions only the electron is involved.

Stronger adsorption of one form would also produce a shift in the cross-over potential since in the immediate

vicinity of the electrode, where rectification takes place, there would be a different ratio of the two forms from that in the "reduction layer". The cross over potential would be reached when equal amounts of the two forms were adsorbed. This alone would not account for the effect of frequency change, but it seems quite possible that the adsorbed form is able to react faster than the unadsorbed one. Results obtained (cross-over potential at the lowest part of wave) with Methylene blue, the leuco form of which is known to be strongly adsorbed on the mercury surface, point in this direction. AC polarographic studies carried out by Mr. Bauer in Dr. Breyer's laboratories (private communication) also show a stronger adsorption of perinaphthenone from alkaline media than from acid ones.

The second wave is prone to the formation of maxima; at higher frequency of alternating voltage desorption of the maximum surpressor appears to take place allowing the maximum to appear.

(5) REDUCTION ON LARGE CATHODES.

(a) Apparatus

For large scale reductions an apparatus similar to that described by Lingane (103) and Pasternak (1) was used; it is shown in fig. 5. A 400 ml gas jar served as the reduction vessel and all connections to it were made through a rubber stopper. The anode compartment, containing a silver electrode immersed in KCl solution, was separated by a

filter paper plugand a thin layer of agar jelly. A similar connection was made (through an H tube and a KCl reservoir) to the saturatedcalomel electrode. There was no noticeable diffusion of perinaphthenone into the plugs. For work in strongly acidic solutions sintered glass plugs were substituted, which unfortunately allowed a certain amount of diffusion. The position, speed and direction of the propeller type glass stirrer were found to influence the maximum possible reduction rate (at the fixed cathode potential) to quite a large extent. The best results were obtained if the stirrer was placed 1 mm above the cathode surface, sucking liquid away from it and rotating at about 1000 r.p.m. When the stirrer was placed closer to the surface, as recommended by Lingane, the mercury was broken up and did not coalesce for an appreciable time; the "cathode surface" was then very small and separated from the rest of the solution by more mercury drops. For this reason a silver cathode was used in the first three reductions until the final method was evolved.

The electrical circuit used was quite simple, two variable resistances acting as controllers for the voltage drop across the cell. The reduction was followed by a milliammeter and a Hydrogen-Oxygen coulometer, but the amount of current passed was checked with the more accurate iodine coulometer. The cathode potential was measured with a vacuum tube voltmeter to an accuracy of 0.02

volts; this was also used to determine the redox potential of the solution; for more accurate work such as determining rate constants a Leeds and Northrup Model K potentiometer was substituted for it.

(b) Method -

The solvent, usually 150 mls of 50% freshly distilled (after refluxing over sodium hydroxide) ethanol with aqueous buffer solution and 10g KCl to improve the conductance, was de-oxygenated by bubbling nitrogen (washed with alkaline pyrogallol and saturated with the solvent used) through it for 30 minutes and finally reduced electrolytically (at a potential above that to be used but below the evolution of hydrogen) till no appreciable current was flowing. The polarographic "neutrality" was then checked by taking a polarogram (with nitrogen flowing over the solution) and the perinaphthenone added as a finely powdered solid. This dissolved after a few minutes' fast stirring and the solution was then repolarographed. Reduction was started and the cathode potential kept constant whilst nitrogen was blown through the solution; its redox potential was checked with a platinum electrode. When the required number of coulombs was estimated to have passed through the solution (H_2,O_2 coulometer) a polarogram was taken and the number of electrons taken up by each molecule calculated from the decrease in the height of the first wave and the number of

coulombs passed through the solution (iodine coulometer). Reduction was then either continued or the mixture ether extracted, the ether extract dried over Sodium Sulphate and evaporated, the product being kept for further examination. The average current density was approx. 3-5 times that of the dropping mercury electrode in a solution of the same concentration of perinaphthenone.

(c) Results and Discussion -

The results are summarised in Tables 21 and 22. In the first ten reductions (Table 21) commercial nitrogen, washed with pyrogallol solution was used to prevent oxidation; it appears that its oxygen content was sufficiently high to re-oxidize the reduction products to a certain extent. That this proceeds very easily was shown by two examples: A small, pale yellow sample which had been reduced in acid solution to the dimer was allowed to stand in an apparently tightly sealed container under nitrogen; sufficient air leaked in overnight to show a distinct orange red layer on top of the solution which slowly moved down. Air was blown for a few minutes through small samples which had been reduced so that no polarograms were obtained; they gave polarograms similar to the original ones (usually with a slightly higher second wave) after prolonged purging with nitrogen. No serious consideration can therefore be given to the number of electrons taken up in these experiments.

The percentage enol (fraction unextractable with ether from alkaline solutions) is also too low as oxidation to ketones probably took place during extraction. The fact that the re-oxidation product is not identical with the original is shown by the polarograms (in Tables 18 and 19) of the two fractions of the first reduction product; sample B, which behaves as an enol during extraction, gives polarograms like an aromatic or unsaturated ketone. Sample A appears to be a mixture, one component showing reduction potentials similar to those of perinaphthenone, the other more negatives ones.

TABLE 21.

REDUCTION ON LARGE CATHODE AT THE FIRST PLATEAU.

No.	pH.	10^3C	Cathode	F.	$\frac{h1a}{h1b}$	$\frac{h2a}{h2b}$	% enol
1	13	10	Ag	6.04	.85	1.5	33
2	2.3	10	Ag	1.9	1	1.5	22
3	2.3	5	Ag	1	.9	1.1	0
4	7	5	Ag	(0.5	.5	1.2)	0
				(1.0	.25	1.0)	
5	13	5	Hg	1.3	1	1.5	16
6	2.3	5	Hg	1.0	.8	1.3	0
7	12	3	Hg	2.0	1	2.8	30
8	3	1.3	Hg	(1	.85	1.3)	
				(2	.8	1.3)	
				(4	.3	.4)	n.d.
				(6	.1	.1)	
9	7	1.3	Hg	(1	.44	1.16)	n.d.
				(2	.23	.75)	n.d.
10	12	1.3	Hg	(1	.88	1.4)	15
				(2	.96	1.2)	
				(4	.88	2.7)	
				(6	.68	3.3)	
				(8	.46	1.1)	
				(10	.26	0.9)	

h1a is the height of the first wave after reduction
h2a is the height of the second wave after reduction
h1b is the height of the first wave before reduction
h2b is the height of the second wave before reduction
F = Faradays passed per g mole

TABLE 22.

REDUCTION ON LARGE MERCURY CATHODE.

No.	10^3C	P	pH	F	E	$\frac{h1a}{h1b}$	$\frac{h2a}{h2b}$
11	1.3	1	2.3	0.9	1.0	.1	.1
13	1.3	1	2.3	0.95	1.02	.07	.1
12	1.3	1	12	(1	2.0	.5	1.0
				(2	2.5	.2	1.0
14	1.3	1	13	2.15	2.5	.2	.8
15	1.3	1	12	2.2	3.6	.38	.66
17	1.3	2	2.3	1.6	1.6	.02	.04
19	1.3	2	2.3	1.45	1.7	.16	.3
16	1.3	2	12	4.0	4.2	.05	.1
18	1.3	2	12	1.9	2.0	.05	.05
20	1.3	2	12	2.6	2.9	.12	.12
21	5	1	St.acid	1.2	1.5	.2	1.0
22	2.5	1	St.acid	1.1	2.0	.45	1.0

Solvent for 21 was 10% $HClO_4$ in glacial acetic acid.
Solvent for 22 10% 10N HCl in glacial acetic acid.
F is the number of Faradays per g mole passed through the solution
E is the number of electrons taken up per molecule (calculated from F by making allowance for the unreduced material shown by $\frac{h1a}{h1b}$)
P denotes the potential at which reduction is carried out (i.e. after the first or second step).

In reductions 11-22 (shown in Table 22) specially purified nitrogen was used and no re-oxidation took place during electrolysis. The results therefore will be similar to those obtained polarographically. At pH2.3 the free radical dimerizes irreversibly, the product remaining an alcohol or phenol. Molecular weight determinations (elevation of the boiling point of acetone detailed in

appendix 3) also show dimerization to have occurred. Reduction at the potential of the second wave allows the uptake of two electrons in competition with dimerization, molecular weight determinations showing predominantly a monomer. In alkaline solutions disproportionation rather than dimerization of the free radical ion takes place, as shown by the number of electrons taken up and the molecular weight of the product. Weiss (104) has pointed out that free radicals with a higher dipole will tend to disproportionate rather than dimerize as collisions between their positive and negative ends will aid electron transfer rather than electron sharing. A slower secondary re-arrangement of the enol (or naphthol) to an aromatic or unsaturated ketone (as shown in fig.11) or possibly further disproportionation to the tetrahydro-product appears to take place under alkaline conditions allowing further reduction to a total uptake of 4 electrons. The first alternative would also account for the frequent increase in the height of the second wave (compared to the height of the first one) obtained in the products of large scale reduction.

In strongly acid solutions disproportionation of the free radical also takes place; probably the free radical with the unpaired electron in the centre is formed first as suggested by Clar (5) (see fig.1),which may tend to disproportionate rather than form the weakened covalent link at an angle of 90^{0} degrees to the other three bonds.

(6) DETERMINATION OF THE DECOMPOSITION RATE CONSTANT OF THE FREE RADICAL

If the first step is electrochemically reversible, an inert electrode immersed into the solution containing perinaphthenone and the initial reduction product should show their relative concentrations according to the Nernst equation. When the reduction is stopped the rate of decomposition of the free radical can then be measured. An alternate method is to equate its rate of formation (given by the electron uptake) with the rate of decomposition when it reaches a steady concentration (as shown by the redox potential of the solution). In each case the assumption has to be made that the reduction is also polarographically fully reversible, i.e. that the standard redox potential is equal to the half wave potential. In alkaline solution a qualitative visual estimate can also be made from the rate with which the dark orange colour of the free radical disappears.

The method used therefore was to polarograph, then to reduce at the first plateau until a steady redox potential was reached, and finally to take readings of the redox potential at regular intervals; under an atmosphere of Nitrogen in a thermostate at 25°C.

In alkaline solution there was no change in the redox potential of the stirred and unstirred solution; it can therefore be considered reversible (105). The results obtained (some calculations are shown in appendix 4) showed

the expected second order reaction giving rate constants of 2×10^2, 6×10^2, 6×10^2 and 1×10^3 g mole^{-1} l sec^{-1}.

In neutral and acid conditions the potential also dropped as reduction was stopped, but changed when the solution was stirred. The Nernst equation will therefore not hold (105) and it is impossible to calculate the rate constant as the concentrations are not known. As the rate of change of potential was distinctly higher than in alkaline solutions it can be assumed that the dimerization rate is faster. This is to be expected as there will be a certain amount of repulsion between the negative ions; another contributing structure to the resonance hybrid with the unpaired electron on the oxygen (similar to the 9-methoxy-phenanthrene-10 oxyl radical (106) will also be possible, under alkaline conditions

(7) DETERMINATION OF THE DISSOCIATION CONSTANT OF THE CONJUGATE ACIDS.

Hammett (107) defined the H_o function as a measure of the proton availability in strongly acid media where the pH scale no longer applies as

$$H_o = -\log a\, H^+ + \log \left(\frac{\gamma\ (AH)+}{\gamma\ A} \right)$$

and determined its value at varying concentrations of strong acids.

An alternate formulation is

$$H_o = pK_{(AH)^+} + \log \frac{cA}{c\ (AH)+}$$

where $K_{(AH)^+}$ is the dissociation constant of the protonated acid.

Thus if a weak base, such as a ketone, is placed into a solution of known H_o value, it will compete with the solvent for protons and the formation of its conjugage acid BH^+ will be governed by the equation

$$H_o = pKa + \log \frac{C\ B}{C\ BH^+}$$

where pKa is the dissociation constant of its conjugate acid BH^+.

If the base is far more soluble in non-polar solvents than in polar ones, it should remain in the lipoid layer if this is shaken with acid, where the protonated ketone will dissolve. By comparing the colour intensities in both layers using various acid concentrations it is thus possible to

determine the pKa value of the ketones conjugate acid. This was done using 0·001M solutions of ketones (0·0002M of perinaphthenone carboxylic acid because of its low solubility) and sulphuric and perchloric acids of various concentrations. The H_o value of the acid which was estimated (visually) to have transformed half the ketone tested to its conjugate acid was taken as the pKa value. It was hoped to carry out more accurate determinations using a spectrophotometer but this was unavailable.

The pKa values obtained (results from the different acids agreeing with ±0·2 units) are shown below.
(Hammett (107) gives a value of -5·61 for chalcone and -6·03 for acetophenone)

Perinaphthenone -7	-1·9
6 - Hydroxyperinaphthenone -7	-2·3
7 - Perinaphthenone - 9 - carboxylic acid	-3·0
Benzanthrone	-4·5
Chalcone	-5·5

SECTION F.

CONCLUSIONS.

The first stage of the reduction of a semi-aromatic ketone at the dropping mercury electrode proceeds in a similar manner to that of a β,γ unsaturated ketone yielding the free radical. This is stabilized by a possible distribution of the unpaired electron over the whole molecule, compared to its predominant localisation at the γ carbon atom of the unsaturated ketone. The resonance stabilization decreases the free energy difference between the free radical and the semi-aromatic ketone thus making the reversible reduction easier. A similar stabilization applies to the distribution of the positive charge of the carbonium ion formed by the action of strong acid; the dissociation constants of the conjugate acids of chalcone, benzanthrone and perinaphthenone, should and do therefore follow the same order as the first half wave potentials. (Ka-5·5, -4.5, -1.9, $E_{\frac{1}{2}}$(pH5) .82, .77, .65). The initial reduction is also aided by electron attracting groups decreasing the electron density around the carbon atom to be reduced and is made more difficult by both electron donating groups and the hydroxy group in the peri position stabilizing the carbonyl group by hydrogen bonding. The reversibility of the first step in alkaline conditions is proved by the attainment of an oxidation reduction potential by a platinum electrode immersed into a

solution being reduced at its plateau potential.

The free radical produced from perinaphthenone dimerizes in dilute acid media like chalcone. Under alkaline conditions it disproportionates in a second order reaction of approx. $g\text{-mole}^{-1}\ l\ sec^{-1}$.

The second stage of the reduction process will depend largely on the distribution of the free electron. Benzalacetophenone (where the free electron is nearly localised at the γ carbon atom) will give the enol which will quickly tautomerize to the benzylacetophenone (1). In the hydroxyperinaphthyl free radical rings B or C will tend to be reduced producing naphthols showing the preference of the free electron for ring A due to the higher resonance stabilization of a naphthol compared to a naphthalene alcohol. In alkaline large scale reductions these products will rearrange or disproportionate, allowing a total uptake of four electrons so that ring B or C will be fully saturated.

Similar results are obtained in chemical reductions of benzanthrone and methoxyperinaphthenone and in Grignard reactions.

If another double bond is conjugated to carbon atom 9 (the equivalent of the γ carbon atom of benzalacetophenone) the chance of the unpaired electron to be in this position is increased and the naphthalene enol, which will tautomerize to the naphthyl ketone will tend to be formed. This will then give a third reduction step analogous to that of benzylacetophenone mentioned above.

Whilst the stability of the free radical produced from Benzanthrone is the highest of all investigated in this work (it is not reduced at the dropping mercury electrode before hydrogen is evolved) the difference in free energy between it and the parent ketone is larger than that in the perinaphthenone system. This is due to the higher resonance stabilization of benzanthrone compared to perinaphthenone.

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APPENDIX I.

CHARACTERISTICS OF CAPILLARIES.

	hmm	mg/sec	t sec.	$m^{2/3} t^{1/6}$	$\frac{m^{2/3} t^{1/6}}{\sqrt{h}}$
(A)	300	1.37	2.9	1.42	
(B)	200	1.08	6.65	1.44	.102
	300	1.73	4.33	1.84	.106
	400	2.24	3.22	2.08	.104
	500	2.88	2.61	2.37	.106
	600	3.53	2.14	2.62	.107
(C)	300	7.72	2	4.4	
(D)	400	id of 0.004 M. $Pb(NO_3)_2$ at 23°C			= 18.0 μa
		calc. at 25°C			= 18.7 μa

$D^{\frac{1}{2}}Pb$ $(25^{\circ}C) = 3.12 \times 10^{-3}$

$$m^{2/3} t^{1/6} (D) = \frac{18.7}{605 \times 4 \times 2 \times 3.12 \times 10^{-3}} = \frac{18.7}{16.1} = 1.16$$

check (A) id of 0.004 M $Pb(NO_3)_2$ at 22°C = 21.6 μa

calc. at 25°C = 22.4 μa

$$m^{2/3} t^{1/6} = \frac{22.4}{16.1} = 1.39$$

APPENDIX 2.

DETERMINATION OF "n".

10^3c	R 10^3ohms	K 10^{-3}r.o.	K corr. 10^{-3}r.o	Λ_c	pH
40	1.05	2.53	2.53	63.6	6.9
20	1.99	1.33	1.33	66.8	6.9
10	3.93	0.672	0.669	66.9	6.8
5.0	7.70	0.345	0.340	68.4	6.8
2.5	15.0	0.178	0.175	70.0	6.9
1.25	28.5	0.092	0.089	71.2	7.0
0.63	54.9	0.048	0.045	72.5	7.0
0.31	101	0.026	0.023	73	7.2
0.16	180	0.015	0.011	73	7.2

conductivity water $R = 8 \times 10^5$ ohms

N/10 K Cl $R = 205.5$ ohms, cell constant = 2.65

$\Lambda_o = 73$, $\lambda^+_{Na} = 51$ $\lambda^- = 22$

$D^{\frac{1}{2}} = 2.4 \times 10^{-3}$ $D_o = 2.67 \times 10^{-7}$ $\lambda^- = 5.9 \times 10^{-6}$

id 0.004 M Pb^{**} in 0.1N NH_4NO_3 = 18.0 μA

id (1) 0.004M phone. carbox. in 0.2N N_aOH = 8.0 μA

$$\frac{id\,Pb^{**}}{id\,(1)} = \frac{2K\,D^{\frac{1}{2}}Pb^{**}}{nK\,D^{\frac{1}{2}}(p.\ crbx)} = \frac{3.12 \times 2}{2.4\ n} = \frac{18.0}{8.0}$$

$$n = 1.12$$

Sample: 0.001 M perinaphthenone in 200 ml

0.01N NaOH, 50% Ethanol

Reduction Rate 1.5 milliamps.

$E_{\frac{1}{2}}$ = -0.928V, E (Pt) during reduction -0.825V.

$$\log (\text{conc. F.R.}) = \frac{0.825-0.928-0.18}{0.06} = -4.75$$

conc. FR. during reduction = 1.8×10^{-5} g moles/l

Formation Rate of F.R. = 1.5×10^{-8} g moles/sec/200 ml

$$K = \frac{7.5 \times 10^{-8}}{3.2 \times 10^{-10}} = 2 \times 10^{2} \text{ g moles}^{-1} \text{ l sec}^{-1}$$

T min	-E	log (a-x)	10^6(a-x)	10^6x	log x	log t min	log K sec
0.0	0.816	-4.90	12.5	--	--	--	--
0.5	0.804	-5.10	7.9	4.6	-5.35	$\bar{1}$.70	3.27
1.5	0.799	-5.19	6.5	6.0	-5.22	0.18	2.88
2.5	0.798	-5.22	6.0	6.5	-5.19	0.36	2.79
5.0	0.796	-5.25	5.6	6.9	-5.16	0.70	2.61
7.5	0.791	-5.32	4.8	7.7	-5.12	0.88	2.63
10.0	0.776	-5.38	4.1	8.4	-5.08	1.00	2.71
13.0	0.760	-5.55	1.4	11.1	-5.05	1.11	3.00

$K = 6 \times 10^{2}$ g moles^{-1} l sec^{-1}.

APPENDIX 4.

CALCULATION OF DECOMPOSITION RATE OF THE FREE RADICAL.

An example of the calculation of decomposition rates is given below

Sample: 200 ml 0.1M NaOH 0.05 M KCl 0.001 M Perinaphthenone in 50% Ethanol

Reduction rate = 6.5 milliamps

Steady Redox potential during reduction = -0.83 V (S.G.E.)

$E\ \frac{1}{2}$ (polarograph) = -0.937 V (S.G.E.), $\log C(F.R.) = \frac{-.83 - .937 - .18}{.06} = -4.$

K from formation rate (assuming bi-molecular decomposition)

$$= \frac{\text{g moles decomposed/l/sec}}{\text{g moles}(F.R.)^2/\ l^2}$$

$$= \frac{\text{Amps} \times 5}{96500 \times C^2} = \frac{6.5 \times 5 \times 10^{-3}}{2.5 \times 10\text{-}10 \times 96500}$$

$$= 1.3 \times 10^3 \text{ g mol}^{-1}\ \text{l sec}^{-1}$$

$$K \text{ from decomposition} = \frac{x}{ta(a - x)}$$ where x is the amount decomposed

a = initial conc. (t = 0) and (a - x) = reactant conc.

T min	-E	$\log_{(a-x)}$	$10^6(a-x)$	$10^6 x$	log x	log T sec	log K
0	.817	-4.97	10.7	0	-	-	
2	.800	-5.33	4.7	6.0	-5.22	2.08	3.00
3	.784	-5.61	2.5	8.2	-5.09	2.26	3.13
5	.780	-5.68	2.1	8.6	-5.06	2.48	3.08
6	.770	-5.82	1.5	9.2	-5.04	2.56	3.19

Average log K = 3.1 1.1×10^{-3} g mole^{-1} l sec^{-1}

APPENDIX 3.

DETERMINATION OF THE MOLECULAR WEIGHT OF REDUCTION PRODUCTS.

The elevation of the boiling point of acetone in a semi-micro boiler by the addition of the reduction products bracketed between naphthalene samples were used to determine their approximate molecular weights.

Sample	mg	ΔT^{o}	$K = \frac{128 \Delta T}{mg}$	$MW = \frac{K\ mg}{\Delta T}$
Naphthalene	13.8	.052	.48	
13	12.3	.021		280
Naphthalene	16.8	.060	.46	
Naphthalene	8.8	.035	.51	
17	15.6	.042		190
Naphthalene	13.7	.055	.52	
Naphthalene	11.4	.045	.50	
15	13.9	.090		170
Naphthalene	15.2	.054	.46	
Naphthalene	12.5	.050	.51	
16	11.0	.030		180
Naphthalene	15.6	.058	.48	